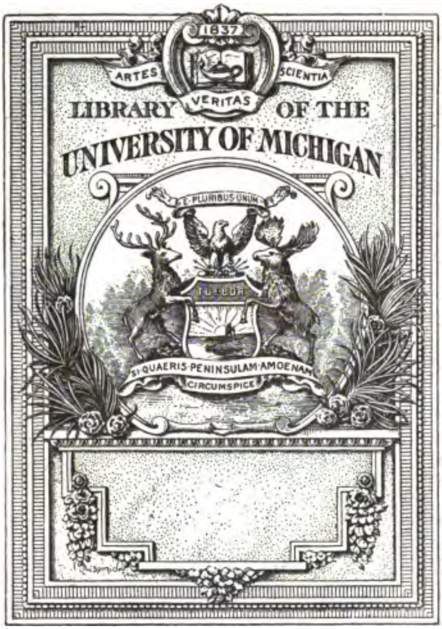
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LECTURE NOTES

ON

QUALITATIVE ANALYSIS.

BY

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PREFACE.

ALTHOUGH the advantages to be gained by teaching qualitative analysis by lecture are sufficiently obvious, it is a serious disadvantage to the student that the necessity of taking proper notes often prevents him from seeing what takes place upon the lecture table. This little book was intended to give concisely the most important facts essential to intelligent work in the laboratory, and thus give the student more leisure for observation in the lecture room.

A comparative description of those compounds of bases and acids which are commonly found or used in analysis is first given, and afterwards a method of separation which experience has proved to be sufficiently simple and accurate, is briefly explained. This method of procedure from the properties of compounds to the methods of separation will also serve to show the way in which the more difficult problems of analysis must be solved.

No tables for analysis have been given, since their use is of questionable advisability, and, if used, are much better drawn up by the student himself.

Symbols have been used throughout for reagents for the sake of brevity, those used in solution being distinguished by the addition of "Aq."

For the sake of simplicity, water has often been omitted from the formulæ of compounds, inasmuch as the number of molecules of water

is largely dependent upon circumstances, and its presence is of minor importance.

Of a compilation of this sort, it is hardly necessary to add that its facts are taken mainly from the text-books of Fresenius and Rose, and the Dictionary of Solubilities of Storer.

CAMBRIDGE, Sept. 1, 1874.

INTRODUCTION.

QUALITATIVE ANALYSIS is that branch of chemistry which treats of the recognition of elements or their compounds. It demands a thorough study and comparison of the several elements and their compounds, of the phenomena exhibited by them under various conditions, and the determination of the particular conditions essential to the manifestation of each. It is advisable, at first, to take into consideration only the more common compounds, and to leave for subsequent study all rare elements and all but a few of the compounds of carbon (organic substances).

The phenomena exhibited by a substance under various conditions are termed its *reactions*. The conditions under which reactions are studied may be divided into two classes: those dependent upon solution, and those independent of it; the two modes of examination are known as the wet and the dry way. In either case any known substance which is used in effecting a reaction is called a *reagent*.

Reactions in the dry way are dependent upon volatilization, or chemical change effected by heat. The nature of these changes will be sufficiently clear after a study of the reactions described in the preliminary examination.

In the wet way a reagent is used to effect solution or to determine a metathesis. Experience has shown that when the solutions of two substances are mixed, and a compound insoluble under the existing conditions can be formed by metathesis, that this insoluble compound is formed; or when a substance volatile under the existing conditions can be formed, that it is formed and escapes. An insoluble substance

separating from solution is called a *precipitate*. If the precipitate settles readily, the liquid may be decanted, or, in any case, it may be separated by filtration, when the liquid is called the *filtrate*. Inasmuch as the completeness of the separation of those substances which are precipitated by a reagent from those which are left in solution depends upon the insolubility of the precipitate, all the conditions which may affect its solubility must be known and considered.

A *general reagent* is used to precipitate a number of substances, a *special reagent* as a test for a single substance. Some special reagents give no precipitate, but cause a change of color. The precipitate thrown down by a general reagent always requires further examination, and it is better to submit to a confirmatory test the precipitate caused by a special reagent. A precipitate or reaction is said to be characteristic when no further test is needed.

There are two things essential to success in qualitative analysis, the accurate observation of phenomena and a correct interpretation of their significance, neither of which can be attained without conscientious work in the laboratory. By studying the reactions of known substances, taking care to observe everything which takes place, however small it may seem, the power of observation will be educated, and it will soon be possible to determine what is accidental and what essential, and experience will show what is the meaning of each reaction observed.

In this book it is supposed that the student already has a good knowledge of general chemistry. Such knowledge is essential, and may be gained by the aid of any good text-book on chemistry. Experience in laboratory work and manipulation, though not absolutely necessary, is on all accounts desirable.*

It is best to begin with the study of the bases, and, taking each group by itself, to compare the properties of the different members. The description of the properties of bases is intended as a guide

* The student may be referred to the following text-books :—

PRINCIPLES OF CHEMICAL PHILOSOPHY. By Josiah P. Cooke, Jr. Boston, 1874.

A MANUAL OF INORGANIC CHEMISTRY : Arranged to facilitate the Experimental Demonstration of the Facts and Principles of the Science. By C. W Eliot and F. H. Storer. New York, 1868.

INORGANIC CHEMISTRY. By T. E. Thorpe. New York, 1874.

in this work. The truth of each important fact given there should be experimentally proved, and reactions seen in the lecture-room should be repeated, if possible.

After a thorough study of the properties of a group of bases, a method of separation should be devised and compared with that given in course of analysis. The members of the group must then be separated from each other, taking care that the facts upon which the method of separation is based are well understood, and the sources of error distinctly recognized. The separation of the group as a whole from the other groups must then be considered, and the conditions necessary for complete separation clearly made out. After the basic groups have been studied in order, and each of the bases can be detected with certainty, a similar method should be followed with acids, taking as a guide the description of the properties of acids, and the methods given for their detection.

The student will then be prepared to make complete analyses. He should begin with simple salts, and proceed gradually to complex mixtures and insoluble substances, in every case proving the presence or absence of each base and acid which he has studied. In the analysis of such compounds the reactions in the dry way should first be observed. Here the significance of each reaction may be learned, as before, by practice upon known substances, or the reactions of a substance may be carefully observed, and its composition afterward determined by analysis in the wet way. The correct interpretation of reactions in the preliminary examination requires long practice. Great care must be taken to distinguish between those reactions which are so decisive that they may be taken as tests for the presence or absence of certain substances, and those which are proofs or indications of presence, if observed, but from whose non-appearance no negative conclusions can be drawn.

As far as practical work is concerned, it will be necessary to give here only a few general directions, and point out a few common errors. Neatness and cleanliness are absolutely necessary. The reagents must be carefully preserved from contamination. The stoppers of the bottles must not be misplaced, nor laid down while the reagent is used. The reagent bottles should

be kept clean and plainly labelled, they should be conveniently arranged, and the order of arrangement never changed.

The quantity of a substance taken for analysis should be small. This facilitates the manipulation, and unless carried to extreme, affords better practice.

Each reagent must be added cautiously, in quantity just sufficient. Too little fails to effect complete precipitation, and separation; too much is often quite as objectionable. If the first few drops of a reagent cause a precipitate, more must be added until a drop allowed to run into the solution gives no further precipitate. The filtrate should also be tested with a few drops of the reagent in confirmation. In using an acid or an alkaline solution the reaction on test-paper will show when an excess has been added. In the use of a few reagents the necessary quantity can be learned by experience alone. In any case, the reagent must be thoroughly mixed with the solution by shaking or stirring.

If a solution is moderately concentrated, the precipitation is usually immediate; but in dilute solutions it often takes place only after some time. If separation is to be effected, time should be allowed for complete precipitation. Occasionally half an hour, or even several hours, are necessary; but more frequently five or ten minutes will be found sufficient. Heat almost always facilitates precipitation; in a few cases, however, which are mentioned in the course of analysis, a reagent must be used in the cold.

In filtering, the filter must be evenly folded and carefully fitted to the funnel. For rapid filtration a creased or star filter is better, and in any case a hot solution filters more rapidly. Precipitates must be thoroughly washed, though only the first part of the wash water should be saved with the filtrate. If the precipitate is granular and settles readily, it may be advantageously washed by decantation before it is collected on a filter. A precipitate may be removed from the filter with a small spatula, or by washing it off with a stream of water, and removing by decantation most of the water. A precipitate may be readily dried by supporting the filter over a hot sand-bath, either in the funnel or on a triangle.

In fusions the well-dried substances should be intimately mixed in a mortar; the crucible containing the mixture should be supported just

above the point of the blue cone of the lamp flame. The removal of the fused mass from a platinum crucible is much facilitated by setting it, while cooling, upon a thick, cold bit of metal.

In blowpipe work full time must be allowed for reduction on charcoal. With borax but little substance must be used, and care must be taken to get a good oxidizing or reducing flame, as the case may be.

It is essential that concise and accurate notes should be kept of all laboratory work. They should record the reactions, the conditions under which they take place, and the conclusions drawn from them. In other words, they should give in order what is done, what is observed, and what is inferred. These notes should be taken as the work is done, and are of value only as they are a truthful record of fact.

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QUALITATIVE ANALYSIS.

BASES.

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GROUP II.

Sulphides soluble, carbonates insoluble:

Ba, Sr, Ca, Mg.

GROUP III.

Sulphides not formed in wet way. $(H_4N)_2S$ + Aq precipitates hydrates:

Al_2, Cr_2, *Th*, *Zr*, *G*, *Y*, *E*, *Ce*, *La*, *D*, *Cb*, *Ta*.

GROUP IV.

Sulphides not formed in acid solutions, but precipitated in alkaline:

Fe, Fe_2*, Ni, Co, Mn, Zn, *U*, *V*, *Tl*, *In*.

GROUP V.

Sulphides formed in acid solutions, insoluble in alkaline:

Ag, Hg, Hg_2, Pb, Cu, Cd, Bi, *Rh*, *Os*, *Ru*, *Pd*.

GROUP VI.

Sulphides formed in acid solutions, soluble in alkaline:

As, Sb, Sn, Sn^{IV}, *Au*, *Pt*, *Ir*, *W*, *Mo*, *Te*, *Se*.

* Is precipitated as Fe S.

PROPERTIES OF BASES.

GROUP I. Na, K, Li, H_4N.

Metals.—Na, K, Li. Soft, very fusible, and lighter than water. Oxidize rapidly in air, or in water setting free H_2. H_4N. Known only in combination, as it is decomposed, when set free, into $2NH_3$ and H_2.

Oxides.—Na_2O and K_2O absorb water eagerly from the air, Li_2O unites with water readily, $(H_4N)_2O$ unknown.

Hydrates.—NaOH and KOH are deliquescent, LiOH sparingly soluble, and H_4NOH ~~known only in solution.~~ not Known

Sulphides.—All soluble.

Chlorides.—LiCl is deliquescent, the rest readily soluble. K_2PtCl_6 and $(H_4N)_2PtCl_6$ are quite insoluble in water, or HCl+Aq, more insoluble in alcohol. The other double chlorides with Pt are soluble.

Carbonates.—Li_2CO_3 sparingly soluble, the other neutral carbonates readily soluble, K_2CO_3 deliquescent.

$KHCO_3$ and $NaHCO_3$ are less soluble than the neutral salts, $LiHCO_3$ more soluble.

Sulphates.—Na_2SO_4, $(H_4N)_2SO_4$ and Li_2SO_4 very soluble, K_2SO_4 less so. The acid salts of the form $MHSO_4$ are all more soluble than the neutral.

Chromates.—All soluble. The salts of the form M_2CrO_4 give a yellow solution, of the form $M_2Cr_2O_7$ a red.

Phosphates.—All Na, K and H_4N salts soluble. Na_2HPO_4 + Aq precipitates Li_3PO_4 insoluble in water, quite soluble in H_4NCl+Aq, and soluble in acids.

Oxalates.—All soluble, KHC_2O_4 not readily.

Tartrates.—Salts of the form $M_2C_4H_4O_6$ all soluble. $KHC_4H_4O_6$ and $H_4NHC_4H_4O_6$ are sparingly soluble in cold water. $HC_2H_3O_2$ does not increase the solubility, though they are soluble in mineral acids, or in an alkaline solution. The other acid salts readily soluble.

Cyanides.—Soluble in water, the salts readily decomposed in solution.

Ferrocyanides.—All soluble.

GROUP II. Ba, Sr, Ca, Mg.

Metals.—Harder than metals of Gr. I. Ba, Sr, and Ca oxidize rapidly in air or water, Mg slowly in moist air, or water at 100°.

Oxides.—Combine with water to form hydrates.

Hydrates.—BaO_2H_2 is soluble, SrO_2H_2 less so; CaO_2H_2 sparingly soluble, and the solubility decreased by heat. MgO_2H_2 is insoluble in water, though soluble in solutions of H_4N salts. All are readily soluble in acids. NaOH + Aq precipitates the hydrates of the group; Ba, Sr and Ca hydrates only from concentrated solutions. H_4NOH + Aq precipitates only MgO_2H_2, that partially, or not at all, in presence of H_4NCl.

Sulphides.—BaS, SrS and CaS are soluble; MgS decomposes water, and therefore is not formed in the wet way.

Chlorides.—$BaCl_2$ and $SrCl_2$ readily soluble, $CaCl_2$ and $MgCl_2$ deliquescent. $MgCl_2$ in solution is partially decomposed by evaporation to dryness.

Carbonates.—Carbonates of the form $M''CO_3$ insoluble in water, soluble in acids. $CaCO_3$ and $SrCO_3$ are

slightly soluble in H_4NCl + Aq, $BaCO_3$ more markedly $MgCO_3$ readily. Na_2CO_3 + Aq precipitates Ba, Sr and Ca as carbonates, Mg as basic carbonate. $(H_4N)_2CO_3$ + Aq precipitates Ba, Sr and Ca completely, Mg partially in concentrated solutions, or not at all in presence of H_4NCl. The salts of the form $M''H_2(CO_3)_2$ are soluble; on boiling their solutions the neutral carbonates are precipitated.

Sulphates.—$BaSO_4$ and $SrSO_4$ are insoluble, $CaSO_4$ sparingly soluble in cold water, less in hot, $MgSO_4$ readily soluble. Mineral acids increase the solubility of $BaSO_4$ but slightly, of $SrSO_4$ and $CaSO_4$ very decidedly. In strong H_2SO_4 all these are soluble, forming acid salts $M''H_2(SO_4)_2$, decomposed by water with formation of $M''SO_4$.

Chromates.—$BaCrO_4$ insoluble in water or $HC_2H_3O_2$, soluble in HCl + Aq or HNO_3. $SrCrO_4$ quite soluble in water, readily in $HC_2H_3O_2$, $CaCrO_4$ and $MgCrO_4$ soluble in water.

Phosphates.—Of the three classes of phosphates, those of the form $M''_3(PO_4)_2$ are insoluble; those of the form $M''_2H_2(PO_4)_2$ are practically insoluble in water, though the Ba and Sr salts are markedly soluble and the Ca salt somewhat soluble in H_4NCl + Aq. The salts of the form $M''H_4(PO_4)_2$ are soluble in water. The insoluble salts are soluble in acids. In neutral solution Na_2HPO_4 + Aq precipitates phosphates of the form $M''_2H_2(PO_4)_2$, in an H_4NOH solution Ba, Sr and Ca precipitated in the form $M''_3(PO_4)_2$. Mg is precipitated by Na_2HPO_4 + Aq in presence of H_4NCl and H_4NOH as $Mg_2(H_4N)_2(PO_4)_2$, insoluble in water, though soluble in acids.

Oxalates.—Neutral oxalates of the form $M''C_2O_4$ in-

soluble in water, soluble in mineral acids; MgC_2O_4 is soluble in $H_4NCl + Aq$.

Tartrates.—Neutral salts of Ba, Sr and Ca insoluble in water, soluble in mineral acids, or $NaOH+Aq$; more or less soluble in $H_4NCl+Aq$. $MgC_4H_4O_6$ sparingly soluble in water, readily soluble in $H_4NCl+Aq$.

Cyanides.—Soluble in water, the solutions decomposed by heat.

Ferrocyanides.—$Ba_2Fe(CN)_6$ sparingly soluble, the rest soluble.

GROUP III. Al_2, Cr_2.

Metals.—Al white, ductile, fusible, and does not readily oxidize. It is soluble in $HCl+Aq$, in dilute H_2SO_4, or in NaOH, + Aq with difficulty in HNO_3. Cr very hard and infusible.

Oxides.—Insoluble in water; before ignition they are soluble in acids, after ignition insoluble. Fusion with Na_2CO_3 and KNO_3 converts Al_2O_3 into soluble $Na_6O_6Al_2$, and Cr_2O_3 into Na_2CrO_4.

Hydrates.—Insoluble in water, soluble in acids, or $NaOH+Aq$. Cr_2 precipitated from NaOH solution by boiling as $Cr_2O_6H_6$, Al_2 is not. Both slightly soluble in $H_4NOH+Aq$, the solubility of $Al_2O_6H_6$ diminished by presence of H_4NCl. On heating the solution the dissolved hydrates are precipitated.

Sulphides.—Not formed in the wet way Al_2S_3 decomposes water, liberating H_2S and forming $Al_2O_6H_6$. $(H_4N)_2S+Aq$ precipitates $Al_2O_6H_6$ and $Cr_2O_6H_6$ with evolution of H_2S.[1]

$$(Al_2Cl_6 + 3(H_4N_2)S + 6H_2O + Aq) = \\ Al_2O_6H_6 + 3H_2S + (6H_4NCl + Aq).$$

Chlorides.—Soluble, Al_2Cl_6 deliquescent.

Carbonates.—Normal salts unknown. Na_2CO_3+Aq or $(H_4N)_2CO_3+Aq$ precipitate essentially $Al_2O_6H_6$ and $Cr_2O_6H_6$ with escape of CO_2.[1]

Sulphates.—Soluble. Most commonly found with K_2SO_4 as alums.

Phosphates.—Salts of the form $(M_2)^{VI}H_{12}(PO_4)_6$ are soluble, the other phosphates insoluble in water, soluble in acids or $NaOH+Aq$; the Cr_2 salts precipitated on boiling the NaOH solution.

Oxalates.—The normal Al_2 salt insoluble, the Cr_2 salt soluble.

Tartrates.—Readily soluble in water. From their solutions $Al_2O_6H_6$ and $Cr_2O_6H_6$ cannot be precipitated.

Cyanides.—$Cr_2(CN)_6$ insoluble in water, slowly soluble in $KCN+Aq$.

GROUP IV. Fe, Ni, Co, Mn, Zn.

Metals.—Fe, Ni, Co, Mn, hard, fuse only at high temperatures, Zn soft, readily fusible, boils at red heat. Mn and Fe oxidize readily in moist air, Co and Ni do not. All soluble in acids.

Oxides.—All insoluble in water, soluble in acids, though FeO and Fe_2O_3 dissolve very slowly after ignition. MnO_2 dissolves in $HCl+Ag$ with evolution of Cl_2.[2]

Hydrates.—Insoluble in water, soluble in acids. FeO_2H_2, white, rapidly turning green or black, and MnO_2H_2,

[1] $(Al_2Cl_6+3Na_2CO_3+3H_2O + Aq) =$
$Al_2O_6H_6+3CO_2+(6NaCl + Aq)$.

[2] $(MnO_2 + 4HCl+Aq)=(MnCl_4 + 2H_2O+Aq)$. The solution then gently heated; $(MnCl_4+Aq)=(MnCl_2+Aq)+Cl_2$.

flesh colored, turning brown, are soluble in $H_4NCl+Aq$; NiO_2H_2, pale green, and CoO_2H_2, pink, are soluble in $H_4NOH+Aq$ or $H_4NCl+Aq$; ZnO_2H_2, white, is soluble in $H_4NOH + Aq$, $NaOH + Aq$ or $H_4NCl + Aq$. $H_4NOH + Aq$ and $NaOH + Aq$ precipitate the hydrates,—with Co a blue basic salt in the cold, but the hydrate on boiling. $Mn_2O_4H_2$, brown, $Ni_2O_6H_6$, black, CoO_6H_6, black, and $Fe_2O_6H_6$, red brown, are insoluble in water or $H_4NCl+Aq$, but soluble in acids.

Sulphides.—Insoluble in water or in solutions of the hydrates or sulphides of Gr. I. When moist they are oxidized upon exposure to the air, some of them, at least, turning into soluble sulphates. FeS, black, MnS, flesh colored, soluble in dilute acids; ZnS, white, soluble in dilute mineral acids, insoluble in $HC_2H_3O_2$; NiS, black, CoS, black, insoluble in cold dilute acid, soluble in strong hot $HCl+Aq$ or HNO_3. The sulphides are not precipitated by H_2S from acid, or, at best, partially from neutral solutions, except ZnS, which is precipitated from solution in $HC_2H_3O_2$. Fe_2S_3 cannot be formed in the wet way. From solutions of Fe_2 salts $(H_4N)_2S+Aq$ precipitates FeS with separation of S.[1] In acid solutions H_2S converts Fe_2 salts into Fe.[2] $(H_4N)_2S+Aq$ precipitates the other members as hydrated sulphides.

Chlorides.—All readily soluble, $ZnCl_2$ very deliquescent.

Carbonates.—Neutral salts $M''CO_3$ insoluble in water, soluble in acids. $FeCO_3$ soluble, $MnCO_3$ slightly soluble in $H_4NCl+Aq$; $NiCO_3$ and $CoCO_3$ are soluble in

[1] $(Fe_2Cl_6+3(H_4N)_2S+Aq)=2FeS+S+(6H_4NCl+Aq)$.

[2] $(Fe_2Cl_6+H_2S+Aq)=S+(2FeCl_2+2HCl+Aq)$.

$H_4NCl+Aq$ or $H_4NOH+Aq$; $ZnCO_3$ soluble in $NaOH+Aq$, $H_4NCl+Aq$ or $H_4NOH+Aq$. From solutions of Fe_2 salts soluble carbonates precipitate essentially $Fe_2O_6H_6$ with evolution of CO_2. From solutions containing other members of the group Na_2CO_3+Aq precipitates basic carbonates; $(H_4N)_2CO_3+Aq$ precipitates similar basic salts, those of Ni, CO and Zn being soluble in an excess.

Sulphates.—All readily soluble.

Phosphates.—Salts of the form $M''H_4\ (PO_4)_2$ soluble, of the forms $M''_2H_2\ (PO_4)_2$ and $M''_3\ (PO_4)_2$ insoluble in water, soluble in acids, more or less soluble in solutions of the soluble salts of the same member of the group. The Mn salts are soluble in $H_4NCl+Aq$; the Ni and Co salts in $H_4NCl + Aq$ or $H_4NOH + Aq$; the Zn salts in $H_4NCl+Aq$, $H_4NOH+Aq$ or $NaOH+Aq$. Na_2HPO_4+Aq added in excess precipitates members of the group in the form $M_3\ (PO_4)_2$.

Oxalates.—The neutral salts insoluble in water, soluble in acids. The Ni and Co salts readily soluble in $H_4NOH + Aq$; ZnC_2O_4 soluble in $H_4NOH + Aq$, $H_4NCl+Aq$ and $NaOH+Aq$.

Tartrates.—$ZnC_4H_4O_6$ and $NiC_4H_4O_6$ insoluble in water, soluble in acids or $NaOH+Aq$; $MnC_4H_4O_6$ and $FeC_4H_4O_6$ sparingly soluble in water, readily soluble in $NaOH+Aq$; $CoC_4H_4O_6$ and $Fe_2(C_4H_4O_6)_3$ soluble in water, the solutions not precipitated by $NaOH+Aq$, or Na_2CO_3+Aq.

Cyanides.—With the exception of the Fe_2 salt, which is unknown, the cyanides are all insoluble in water and soluble in $KCN+Aq$. $Ni(CN)_2$ and $Co(CN)_2$ are also

soluble in H_4NOH + Aq, $Zn(CN)_2$ in H_4NOH + Aq or NaOH + Aq. From the solutions in KCN + Aq $Ni(CN)_2$ and $Zn(CN)_2$ are reprecipitated by neutralizing the KCN with acids. The solutions of the other cyanides in KCN + Aq contain (in the case of Mn and Co only after heating or exposure to air) $K_4Fe(CN)_6$, $K_6Mn_2(CN)_{12}$ and $K_6Co_2(CN)_{12}$ from which acids do not separate the simple cyanides, and from which Fe, Mn and Co cannot be precipitated by ordinary reagents.

Ferrocyanides.—Insoluble in water, decomposed by NaOH + Aq into hydrate of the metal, and $Na_4Fe(CN)_6$. $Zn_2Fe(CN)_6$, white, $Ni_2Fe(CN)_6$, greenish white, $Co_2Fe(CN)_6$, green, $FeK_2Fe(CN)_6$, white, rapidly turning blue, and $(Fe_2)_2(Fe(CN)_6)_3$, blue, insoluble in HCl+Aq; $Mn_2Fe(CN)_6$, reddish white, soluble in HCl + Aq. All are decomposed by heating with H_2SO_4 diluted with $\frac{1}{8}$ its volume of water; HCN evolved, and sulphates left.

GROUP V. Ag, Hg, Pb, Cu, Cd, Bi.

Metals.—Bi brittle, Ag and Pb soft, Cu and Cd harder, Hg liquid at ordinary temperatures. Exposed to the air Ag, Bi and Hg do not oxidize, Pb, Cu and Cd not readily. All but Ag oxidize rapidly at high temperatures. HNO_3 is the best solvent for all, though Cd dissolves in any acid. HCl+Aq does not act upon Ag, Hg, Pb, or Bi, and acts upon Cu only in presence of O. Hot concentrated H_2SO_4 dissolves all but Pb, which it affects but little.

Oxides.—Ag_2O, brown, slightly soluble in water, readily soluble in H_4NOH+Aq, and in solutions of chlorides, cyanides or hyposulphites or in HNO_3. HgO, yellow

or red, and Hg_2O, black, insoluble in water, soluble in HNO_3. PbO, reddish yellow, CuO, black, Cu_2O, red, CdO, brown, and Bi_2O_3, yellow, in solubility are like the hydrates.

Hydrates.—Ag and Hg form no hydrates. PbO_2H_2 is practically insoluble in water, though alkaline to test paper, readily soluble in NaOH+Aq. CuO_2H_2, blue, and $Cu_2O_2H_2$, orange yellow, insoluble in water, slightly soluble in cold NaOH+Aq, soluble in H_4NCl+Aq, or in H_4NOH+Aq. On boiling CuO_2H_2 with NaOH+Aq it is converted into CuO, the small amount dissolved in the cold being precipitated; CdO_2H_2, white, insoluble in water, soluble in H_4NOH+Aq; BiO_5H_3, white, insoluble in water or H_4NOH+Aq. All these hydrates readily soluble in acids.

From solutions containing members of the group NaOH+Aq precipitates Ag, Hg and Hg_2 as oxides, the rest as hydrates, PbO_2H_2 soluble in an excess; H_4NOH+Aq precipitates Ag as oxide, Hg and Hg_2 as insoluble amine compounds, the rest as basic salts, or hydrates, the Ag, Cu, and Cd precipitates being soluble in an excess.

Sulphides.—Insoluble in water, cold dilute acids or solutions of the hydrates or sulphides of Gr. I.; all except HgS and Hg_2S soluble in hot dilute HNO_3. HgS, black, Ag_2S, black, CuS, black, and Bi_2S_3, black, may be completely precipitated from solutions containing HCl + Aq, unless present in very great excess. PbS, black, and CdS, yellow, are not completely precipitated, if much HCl +Aq is present. Hg solutions are precipitated by H_2S first white, then yellow, the color changing to brown red, and

becoming black only with excess of H_2S. The change of color is due to the formation of various insoluble compounds of HgS with undecomposed Hg salt.

Chlorides.—AgCl insoluble in water or acids, soluble in $H_4NOH + Aq$ and in solutions of chlorides, cyanides or hyposulphites. Hg_2Cl_2 insoluble in water but gradually decomposed by boiling with water, $HCl + Aq$ or solutions of chlorides; $H_4NOH + Aq$ converts it into $(Hg_2)_2H_4N_2Cl_2$, black, insoluble in water or $H_4NOH + Aq$. $PbCl_2$ crystalline, sparingly soluble in cold water, still less soluble in dilute $HCl + Aq$, soluble in hot water, in concentrated $HCl + Aq$, or in $NaOH + Aq$. $BiCl_3$ is soluble in a small quantity of water, more water separates BiOCl, white, insoluble in water, soluble in acids. $HgCl_2$ and $CuCl_2$ soluble in water, $CdCl_2$ deliquescent.

Carbonates.—Neutral salts insoluble in water, soluble in acids. Ag_2CO_3 and $CuCO_3$ are readily soluble in $H_4NOH + Aq$, $PbCO_3$ soluble in $NaOH + Aq$. From solutions containing members of the group $Na_2CO_3 + Aq$ precipitates carbonates, generally basic, insoluble in an excess; $(H_4N)_2CO_3 + Aq$ precipitates Hg and Hg_2 as insoluble amine compounds, the rest as carbonates or basic salts, the Ag and Cu salts being readily soluble in an excess.

Sulphates.—$CuSO_4$ and $CdSO_4$ readily soluble; $HgSO_4$ and $Bi_2(SO_4)_3$ decomposed by water, giving insoluble Hg_3SO_6 yellow, and $Bi_2H_4SO_8$ white; Ag_2SO_4 sparingly soluble; $PbSO_4$ insoluble in water, much more soluble in strong acids, readily soluble in $NaOH + Aq$, or in solutions of some H_4N salts, especially $H_4NC_2H_3O_2$ and $(H_4N)_2C_4H_4O_6$.

Phosphates.—The salts of the forms $M''_2H_2(PO_4)$ and $M''_3(PO_4)_2$ are insoluble in water, soluble in HNO_3, many of them in $H_4NCl+Aq$. Ag_3PO_4 and the Cu salts are soluble in $H_4NOH+Aq$, the Pb salts in $NaOH+Aq$. From solutions of the members of the group Na_2HPO_4+Aq precipitates Ag as Ag_3PO_4, and, if added in excess, the rest in the form $M''_3(PO_4)_2$.

Oxalates.—Insoluble in water, soluble in HNO_3. $Ag_2C_2O_4$ and CuC_2O_4 soluble in $H_4NOH+Aq$; PbC_2O_4 soluble in $NaOH+Aq$.

Chromates.—Ag_2CrO_4, brick red, insoluble in water, soluble in $H_4NOH + Aq$, or HNO_3; Hg_2CrO_4, red, and $Bi_2(CrO_4)_3$, yellow, insoluble in water, soluble in HNO_3; $PbCrO_4$ bright yellow, insoluble in water or $HC_2H_3O_2$, soluble in $NaOH + Aq$, with difficulty in HNO_3. $CuCrO_4$, brown, soluble, and $HgCrO_4$ sparingly soluble in water.

Tartrates.—The Cu, Cd and Hg_2 salts sparingly soluble in water, the rest insoluble. $CuC_4H_4O_6$ is readily soluble in $NaOH+Aq$; $PbC_4H_4O_6$ soluble in $H_2C_4H_4O_6+Aq$ or in $NaOH+Aq$.

Cyanides.—$Hg(CN)_2$ soluble in water, the rest insoluble in water, soluble in HNO_3, except AgCN. In $KCN+Aq$ AgCN, $Cu(CN)_2$, $Cd(CN)_2$ are soluble, $Pb(CN)_2$ and $Bi(CN)_3$ insoluble. $KCN + Aq$ added to solutions of Hg_2 salts precipitates Hg, forming $Hg(CN)_2$ in solution.

Ferrocyanides.—$Pb_2Fe(CN)_6$ and $Cd_2Fe(CN)_6$ insoluble in water, soluble in HNO_3; $Ag_4Fe(CN)_6$, white, $Cu_2Fe(CN)_6$, red brown, $Bi_4(Fe(CN)_6)_3$, white, insoluble in acids, or $H_4NOH+Aq$.

GROUP VI. As, Sb, Sn.

Metals.—As and Sb brittle, Sn soft and malleable. As volatilizes without fusion; Sb and Sn fuse readily. As oxidizes at ordinary temperatures, all oxidize readily when heated. As and Sb are hardly attacked by $HCl+Aq$, Sn is easily dissolved. HNO_3 oxidizes all three, Sn and Sb without solution. $HCl+Aq$ with HNO_3 dissolve all.

Oxides.—As_2O_3 sparingly soluble, Sb_2O_3 and Sb_2O_5 slightly soluble in water; the rest insoluble in water. All soluble in $HCl+Aq$ or $HCl+Aq$ with HNO_3. As_2O_3 readily soluble in $NaOH+Aq$. SnO_2 is often insoluble in $HCl+Aq$, but rendered soluble by fusion with NaOH. SnO and Sb_2O_3 heated in air give SnO_2 and Sb_2O_4. As_2O_5 and Sb_2O_5 when heated become As_2O_3 and Sb_2O_4.

Hydrates.—H_3AsO_3 known only in solution or in its salts, H_3AsO_4 soluble. $HSbO_3$ slightly soluble in water. The other hydrates are insoluble in water, soluble in $HCl + Aq$ or $NaOH + Aq$. The Sn^{IV} hydrates more readily soluble in $KOH + Aq$ than in $NaOH + Aq$; one modification of it insoluble in acids, and with great difficulty soluble in $KOH + Aq$.

Sulphides.—Insoluble in water or dilute acids, readily soluble in solutions of the hydrates or sulphides of Gr. I. If dissolved in soluble sulphides they form sulphur salts,[1] or if in solutions of the hydrates, a mixture of sulphur salt with oxygen salt.[2] On adding acid to either of the solutions the original sulphide is reprecipi

[1] $As_2S_3 + (3(H_4N)_2S + Aq) = (2(H_4N)_3AsS_3 + Aq)$.

[2] $As_2S_3 + (6NaOH + Aq) =$
$(Na_3AsO_3 + Na_3AsS_3 + 3H_2O + Aq)$.

tated.[1] SnS dissolved in yellow $(H_4N)_2S$ + Aq precipitated as SnS_2. As_2S_3, yellow, insoluble in strong HCl + Aq, soluble in $(H_4N)_2CO_3$ + Aq; Sb_2S_3 and Sb_2S_5, orange, SnS, brown, SnS_2, yellow, are soluble in strong HCl + Aq, insoluble in $(H_4N)_2CO_3$ + Aq. As^V in acid solution is slowly reduced by H_2S and precipitated as As_2S_3.

Chlorides.—$AsCl_3$, $SbCl_5$, $SnCl_4$ volatile liquids; $SbCl_3$, $SnCl_2$ solids. All decomposed by water; $SnCl_2$ and $SnCl_4$ slowly or when treated with a large amount. $SbCl_3$ gives at once SbOCl insoluble in water, soluble in acids; $AsCl_3$ gives As_2O_3 as the chief product.

Hydrides.—AsH_3 and SbH_3, gaseous, are formed when a soluble As or Sb compound is treated with Zn and dilute H_2SO_4. They are decomposed below red heat into Sb or As and H_2. Passed into $AgNO_3$ + Aq, AsH_3 precipitates Ag and leaves H_3AsO_3 in solution;[2] SbH_3 precipitates $SbAg_3$.[3]

Tartrates.—$(SbO)KC_4H_4O_6$ soluble in water. The presence of $H_2C_4H_4O_6$ in sufficient quantity prevents the precipitation of basic Sb salts by water.

[1] $(2(H_4N)_3AsS_3 + 6HCl + Aq) = As_2S_3 + 3H_2S + (6H_4NCl + Aq)$.
$(Na_3AsO_3 + Na_3AsS_3 + 6HCl + Aq) = As_2S_3 + (6NaCl + 3H_2O + Aq)$.

[2] $AsH_3 + (6AgNO_3 + 3H_2O + Aq) = 3Ag_2 + (6HNO_3 + H_3AsO_3 + Aq)$.

[3] $SbH_3 + (3AgNO_3 + Ag) = SbAg_3 + (3HNO_3 + Aq)$.

ACIDS.

GROUP I.

Ba Salts insoluble in water.

1 Acids decomposed in acid solution by H_2S.

M_2CrO_4	H_3AsO_4	M_2SO_3	$\mathit{HIO_3}$
M_3AsO_3		$M_2S_2O_3$	

2. Acids not decomposed in acid solution by H_2S.

a. Ba Salts soluble in HCl + Aq.

H_3PO_4	HF	$H_2C_4H_4O_6$	$\mathit{HPO_3}$
H_3BO_3		M_2CO_3	$\mathit{H_4P_2O_7}$
$H_2C_2O_4$		H_4SiO_4	$\mathit{H_3PO_3}$

b. Ba Salts insoluble in HCl + Aq.

H_2SO_4 $\mathit{H_2SiF_6}$

GROUP II.

Ba Salts soluble, Ag Salts insoluble in water.

HCl	$H_4Fe(CN)_6$	$\mathit{HNO_2}$
HBr	$H_6Fe_2(CN)_{12}$	HClO
HI	H_2S	$\mathit{HClO_2}$
HCN		$\mathit{H_3PO_2}$

GROUP III.

Ba and Ag Salts soluble in water.

HNO_3	$HClO_3$	$HC_2H_3O_2$
	$\mathit{HClO_4}$	$\mathit{HCHO_2}$

PROPERTIES OF ACIDS.

GROUP I. 1. M_2CrO_4, M_3AsO_3, H_3AsO_4, M_2SO_3, $M_2S_2O_3$.

Chromates.—Salts generally insoluble in water, the most important soluble salts being those of Gr. I., Sr, Ca, Mg, and the normal salts of Mn and Zn. The acid is unknown, since it breaks upon liberation from its salts into H_2O and CrO_3; it also gives no salts of the form $MHCrO_4$. If acid be added to a solution of M_2CrO_4 it turns from yellow to red with the formation of a salt of the form $M_2Cr_2O_7$,[1] further addition of acid sets CrO_3 free.[2] If H_2SO_4 is used the CrO_3 separates as a red mass, or in red needles. CrO_3 heated with H_2SO_4 loses oxygen and becomes $Cr_2(SO_4)_3$,[3] with $HCl+Aq$ it gives Cr_2Cl_6 water and Cl_2.[4] Organic matter or reducing agents, like H_2S or SO_2, effect a similar change, $2CrO_3$ becoming Cr_2O_3.[5] In any case the change of CrO_3 to Cr_2O_3 is accompanied by a corresponding change of color from red to green. $BaCrO_4$ and $PbCrO_4$, yellow, insoluble in water or in $HC_2H_3O_2$. Ag_2CrO_4, brick red, soluble in HNO_3 or $H_4NOH+Aq$.

Arsenites.—The salts of Gr. I. are soluble, the neutral salts of the other groups insoluble in water, though many are soluble in $H_4NCl+Aq$. The acid is unknown,

[1] $(2K_2CrO_4 + H_2SO_4 + Aq) = (K_2Cr_2O_7 + K_2SO_4 + H_2O + Aq).$

[2] $(K_2Cr_2O_7 + H_2SO_4+Aq) = (2CrO_3 + K_2SO_4 + H_2O + Aq).$

[3] $4CrO_3 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 6H_2O + 3O_2.$

[4] $(2CrO_3 + 12HCl + Aq) = (Cr_2Cl_6 + 6H_2O + Aq) + 3Cl_2.$

[5] $(2CrO_3 + 6HCl + 3H_2S + Aq) = (Cr_2Cl_6 + 6H_2O + Aq) + 3S.$

although acid salts of the forms MH_2AsO_3 and M_2HAsO_3 are known. From acid solutions of all salts H_2S readily precipitates As_2S_3 yellow. Oxidizing agents convert the salts into arseniates. $Cu_2H_2(AsO_3)_2$ is green, insoluble in water, soluble in acids, and soluble in $NaOH + Aq$. On warming the NaOH solution $Cu_2O_2H_2$, orange yellow, is precipitated, Na_3AsO_4 being left in solution. $Mg_3(AsO_3)_2$ and $Ba_3(AsO_3)_2$ insoluble in water, soluble in acids, or $H_4NCl + Aq$; Ag_3AsO_3, pale yellow, insoluble in water, soluble in $H_4NOH + Aq$ or HNO_3.

Arseniates.—The salts resemble the phosphates closely. Of the neutral salts only those of Gr. I. are soluble. The acid is solid, soluble in water. From acid solutions of its salts H_2S at first precipitates nothing, but on long standing, or more quickly on warming, it is reduced and As_2S_3 is precipitated. SO_2 reduces it quite rapidly to arsenious acid with formation of H_2SO_4; H_2S then at once precipitates As_2S_3. $Ba_3(AsO_4)_2$ and $Mg_3(AsO_4)_2$ are insoluble in water, soluble in acids. Ag_3AsO_4, red brown, insoluble in water, soluble in $H_4NOH + Aq$ or HNO_3. $Mg_2(H_4N)_2(AsO_4)_2$, insoluble in water or $H_4NCl + Aq$, soluble in acid, is formed when $H_4NOH + Aq$, $H_4NCl + Aq$ and $MgSO_4 + Aq$ are added to aqueous solutions of arseniates. A solution of $(H_4N)_2MO_4$ in HNO_3 gives no precipitate in acid solutions of arseniates in the cold, but gives a yellow precipitate on boiling.

Sulphites.—The neutral salts are all insoluble or sparingly soluble in water; of the acid salts many are soluble, though many are decomposed by boiling their solutions, neutral salts being formed. The acid is un-

known. From its salts stronger acids liberate SO_2 soluble in water; in this solution H_2S forms $H_2S_5O_6$ with separation of S. SO_2 is a powerful reducing agent but is itself reduced by nascent H with formation of H_2S.[1] $BaSO_3$ is insoluble in water, soluble in HCl + Aq; from this solution Cl_2 or Br_2 precipitate $BaSO_4$.

Hyposulphites.—Most of the salts are soluble in water. The acid is unknown. Stronger acids liberate from its salts SO_2 and S. The same decomposition[3] takes place when HCl+Aq is added to solutions of its salts, though slowly in dilute solutions. With H_2S in acid solutions, or with nascent hydrogen the reactions are the same as with the sulphites. BaS_2O_3 insoluble in water soluble in HCl+Aq. $Ag_2S_2O_3$, white, insoluble in water, soluble in solutions of hyposulphites; blackens on heating, Ag_2S being formed. PbS_2O_3, insoluble in water, soluble in solutions of hyposulphites, forms PbS on heating.[4]

GROUP I. 2. (a) H_3PO_4, H_3BO_3, $H_2C_2O_4$, HF, M_2CO_3, H_4SiO_4, $H_2C_4H_4O_6$; (b) H_2SO_4.

Phosphates.—Salts of the forms M_3PO_4 and M_2HPO_4 insoluble except those of Gr. I., salts of the form MH_2PO_4 soluble. All the insoluble salts are soluble in acids, and these solutions are precipitated by H_4NOH +Aq; the precipitate is usually a phosphate of the form M_3PO_4. $Ba_3(PO_4)_2$ and $Ca_3(PO_4)_2$, insoluble in water, are soluble in HCl+Aq and in $HC_2H_3O_2$. Ag_3PO_4, pale yellow, insoluble in water, is soluble in H_4NOH+Aq or

[1] $(Na_2SO_3+2HCl+Aq) = (2NaCl+H_2O+SO_2+Aq)$.
[2] $SO_2+3H_2 = H_2S+2H_2O$.
[3] $(Na_2S_2O_3+2HCl+Aq) = (2NaCl+H_2O+SO_2+Aq)+S$.
[4] $PbS_2O_3 + H_2O = PbS+H_2SO_4$.

HNO_3. From aqueous solutions of the phosphates $MgSO_4 + Aq$, after adding $H_4NCl + Aq$ and $H_4NOH + Aq$, precipitates $Mg_2(H_4N)_2(PO_4)_2$ insoluble in water or $H_4NCl + Aq$, soluble in acids. In acid solutions of the phosphates $(H_4N)_2MO_4$ dissolved in HNO_3 gives a yellow precipitate in the cold, insoluble in water or in dilute acids, if $(H_4N)_2MO_4$ be in excess, readily soluble in excess of phosphate.

Borates.—Only the salts of Gr. I. are readily soluble in water, though many salts insoluble in water are soluble in $H_4NCl + Aq$. The acid is separated from its salts by stronger acids; soluble in water, the solution turning turmeric paper red, best seen when the paper is dried at 100°. This red color is changed to greenish black when moistened with $Na_2CO_3 + Aq$. H_3BO_3 partially volatilized by evaporation of its solution. Its alcoholic solution burns with a green flame. The Ba and Ca salts are insoluble in water, soluble in $HCl + Aq$, $HC_2H_3O_2$ or $H_4NCl + Aq$. The Mg salt readily soluble in $H_4NCl + Aq$.

Oxalates.—Almost all the neutral salts, except those of Gr. I. are insoluble in water, soluble in acids. H_4NOH precipitates the acid solutions of many of the salts insoluble in water, those of Ba, Sr and Ca completely. All the salts are decomposed by ignition; the residue consists of carbonate, oxide or metal. The acid, readily soluble in water, is decomposed when heated by itself or with strong H_2SO_4 into CO_2, CO and H_2O.[1] With the dry salts H_2SO_4 gives the same reaction, first setting the acid free, then decomposing it. The acid or its salts warmed with

[1] $H_2C_2O_4 = H_2O + CO_2 + CO$.

dilute H_2SO_4 and MnO_2 give off CO_2, $MnSO_4$ and water being formed.[1] BaC_2O_4 is insoluble in water, soluble in $HCl + Aq$. CaC_2O_4 is insoluble in water or $HC_2H_3O_2$, soluble in $HCl + Aq$. $Ag_2C_2O_4$ insoluble in water, soluble in $H_4NOH + Aq$ or HNO_3, is decomposed with explosion on ignition, Ag being left. The salts of Gr. II. are decomposed on boiling with a concentrated solution of Na_2CO_3 with formation of the corresponding carbonates and $Na_2C_2O_4$ in solution.

Fluorides.—Salts of Gr. I. readily soluble, as also Al_2F_6, Cr_2F_6, Fe_2F_6, AgF, HgF_2. The rest are sparingly soluble or insoluble in water. HF is liberated from its salts by strong H_2SO_4 as a gas readily soluble in water, the solution characterized by its power of dissolving SiO_2 or its compounds (glass). A fluoride mixed with silicates or SiO_2 gives, on heating with strong H_2SO_4, SiF_4 fuming in the air, and giving with water H_4SiO_4, gelatinous.[2] Fluorides not decomposed by H_2SO_4 must be fused with mixed Na_2CO_3 and K_2CO_3. BaF_2 and CaF_2, as precipitated, are gelatinous and transparent, soluble in hot $HCl + Aq$, though with difficulty, soluble in $H_4NCl + Aq$.

Tartrates.—The neutral salts of Grs. I. and III. as well as of Fe_2 and Co readily soluble in water. The acid is very soluble in water, and its presence prevents partially or wholly precipitation with $NaOH + Aq$, $H_4NOH + Aq$, $Na_2CO_3 + Aq$, or $(H_4N)_2CO_3 + Aq$. The acid and its salts char on heating, giving off an odor like

[1] $(H_2C_2O_4 + H_2SO_4 + Aq) + MnO_2 = (MnSO_4 + 2H_2O + Aq) + 2CO_2$.

[2] $(3SiF_4 + 4H_2O + Aq) = H_4SiO_4 + (2H_2SiF_6 + Aq)$.

burnt sugar. $BaC_4H_4O_6$ insoluble in water, soluble in $HCl + Aq$ or $H_4NCl + Aq$. $CaC_4H_4O_6$ insoluble in water, soluble in HCl or $HC_2H_3O_2$, quite soluble in $H_4NCl + Aq$, readily soluble in cold $NaOH + Aq$, reprecipitated gelatinous on boiling; $Ag_2C_4H_4O_6$, white, insoluble in water, soluble in $H_4NOH + Aq$ or HNO_3; blackens immediately on boiling from separated Ag. $KHC_4H_4O_6$ is sparingly soluble in cold water, $HC_2H_3O_2$ or $H_2C_4H_4O_6 + Aq$ readily soluble in mineral acids or solutions of hydrates of Gr. I.

Carbonates.—The neutral salts are all insoluble in water, except those of Gr. I.; the acid salts are generally soluble, though, if their solutions are boiled, all but those of Gr. I. are decomposed, and neutral salts precipitated. The acid is unknown, since it breaks up upon liberation from its salts into water and CO_2, a gas heavier than air, quite soluble in water. CO_2 gives with CaO_2H_2 $CaCO_3$, white. $BaCO_3$ insoluble in water, soluble in acids. Ag_2CO_3, white, insoluble in water, soluble in $H_4NOH + Aq$ or HNO_3.

Silicates.—The silicates of Gr. I. are alone soluble in water; many of the insoluble salts are decomposed by strong acids with the separation of H_4SiO_4. When the acid is liberated from its salts by acids, the greater part generally separates in a gelatinous form, though more or less remains in solution. If such an acid solution is evaporated to dryness, all its Si is left as a hydrate, insoluble in water or acids (except $HFl + Aq$). H_4SiO_4 when once formed is insoluble in water or acids (except $HF + Aq$), though soluble in $NaOH + Aq$, and reprecipitated from this solution by $H_4NCl + Aq$. It loses water readily,

and on ignition SiO_2 is left insoluble in a bead of microcosmic salt (NaH_4NHPO_4). All silicates are decomposed by fusion with mixed Na_2CO_3, and K_2CO_3. The Ba, Ca and Ag salts are insoluble, decomposed by HCl + Aq.

Sulphates.—The normal salts are all soluble, except $BaSO_4$, $SrSO_4$ and $PbSO_4$, insoluble, and $CaSO_4$ sparingly soluble. The acid has great affinity for water, and dissolves with evolution of heat. When strong it blackens organic water. Sulphates, when heated on charcoal with Na_2CO_3 in the inner blowpipe flame, give Na_2S. $BaSO_4$, white, insoluble in water or acids.

GROUP II. HCl, HBr, HI, HCN, $H_4Fe_2(CN)_6$, $H_6Fe_2(CN)_{12}$, H_2S.

Chlorides.—All soluble except AgCl, Hg_2Cl_2 insoluble, and $PbCl_2$ sparingly soluble in water. From its salts H_2SO_4 liberates HCl (with effervescence, if little or no water is present), a gas very soluble in water; H_2SO_4 and MnO_2 evolve Cl_2,[1] a greenish gas, somewhat soluble in water, which bleaches. AgCl insoluble in water, or HNO_3, soluble in H_4NOH + Aq.

Bromides.—Salts soluble except AgBr and Hg_2Br_2. From its salts H_2SO_4 liberates HBr, a gas very soluble in water, but mixed with more or less Br_2; H_2SO_4 and MnO_2 liberate Br_2, a red volatile liquid soluble in water, its vapors red. In solutions of the bromides Cl_2 + Aq liberates Br_2, which colors the liquid red. The Br_2, thus liberated, can all be collected in a little CS_2, in which it is much more soluble than in water. An excess of Cl_2 bleaches the color.

$$2NaCl + 3H_2SO_4 + MnO_2 = 2NaHSO_4 + MnSO_4 + 2H_2O_2 + Cl_2.$$

Iodides.—Soluble except AgI, yellowish white, Hg_2I_2, greenish, HgI_2, red, PbI_2, yellow, and Bi_2I_3, insoluble in water. From its salts H_2SO_4 liberates HI, but it is at once oxidized and I_2 set free. I_2 is almost insoluble in water, readily soluble in CS_2, which it colors violet; soluble, also, in solutions of iodides with a deep brown color. It sublimes with gentle heat, its vapor being violet. Cl_2 liberates I_2 from its salts, an excess of Cl_2 then converts it into colorless ICl_3. I_2 gives with dilute starch paste in a slightly acid solution a deep blue compound of starch and I, bleached by heat or Cl_2. AgI insoluble in water or HNO_3, scarcely soluble in H_4NOH + Aq, soluble in solutions of iodides.

Cyanides.—Salts of Grs. I. and II. and $Hg(CN)_2$ soluble, the rest insoluble in water though many are soluble in solutions of cyanides. HCN is a volatile liquid soluble in water. From the soluble salts even dilute acids liberate the acid; strong H_2SO_4 decomposes it, giving CO. The insoluble salts are all decomposed by ignition. Many of the insoluble salts are decomposed by HCl + Aq, all by strong H_2SO_4. AgCN, white, insoluble in water or dilute HNO_3, soluble in H_4NOH + Aq, or in solutions of cyanides of Grs. I. and II.

Ferrocyanides.—All insoluble in water except the salts of Grs. I. and II. Many of the salts are colored, and all the insoluble salts decomposed by NaOH + Aq or H_2SO_4. $H_4Fe(CN)_6$ is a white solid readily soluble in water. Cl_2 converts $K_4Fe(CN)_6$ in solution into $K_6Fe_2(CN)_{12}$. $Ag_4Fe(CN)_6$, white, insoluble in water, H_4NOH + Aq or HNO_3. $(Fe_2)_2(Fe(CN)_6)_3$, blue, and $Cu_2Fe(CN)_6$, red brown, insoluble in water, or HCl + Aq.

Ferricyanides.—Salts of Grs. I. and II. and Fe_2 soluble in water. Many of the salts are colored, and all insoluble salts decomposed by $NaOH$ + Aq or H_2SO_4. The acid, $H_6Fe_2(CN)_{12}$, is readily soluble in water and converted by reducing agents into $H_4Fe(CN)_6$. $Ag_6Fe_2(CN)_{12}$, orange, insoluble in water, or HNO_3, soluble in H_4NOH + Aq. $Fe_3Fe_2(CN)_{12}$ blue, insoluble in water, or HCl + Aq. $Fe_2Fe_2(CN)_{12}$ soluble in water, the solution brown.

Sulphides.—The salts of Grs. I. and II. soluble, the rest insoluble in water. The salts of Gr. VI. soluble in NaOH + Aq. Most salts attacked by hot HCl + Aq, and all by HCl + Aq with HNO_3. Solution is effected by HCl + Aq with liberation of the acid H_2S, a gas somewhat soluble in water; by HNO_3, or HCl + Aq with HNO_3, with separation of S, which by boiling is slowly oxidized to H_2SO_4. Ag_2S, black, insoluble in H_4NOH + Aq, soluble in hot HNO_3.

GROUP III. HNO_3, $HClO_3$, $HC_2H_3O_2$.

Nitrates.—Normal salts all soluble in water. From its salts H_2SO_4 liberates HNO_3, a fuming liquid, perfectly soluble in water. By the action of HNO_3 upon Cu, NO is formed[1], a colorless gas, which with the O of the air forms NO_2, orange red. NO is also soluble in a concentrated solution of $FeSO_4$, forming a solution colored black, brown, or reddish, according to its concentration. On heating the solution NO is set free. All the salts deflagrate when heated on charcoal, and all are decomposed by ignition.

Chlorates.—Normal salts all soluble in water. H_2SO_4

[1] $3Cu + (8HNO_3 + Aq) = (3Cu(NO_3)_2 + 4H_2O + Aq) + 2NO.$

added to the chlorates liberates Cl_2O_4, a yellow green gas, smelling like Cl_2 and bleaching, the H_2SO_4 becoming yellow. Heat must be avoided or the decomposition is accompanied by explosion. $HCl + Aq$ liberates a gas of similar color and odor, Cl_6O_{13}. $HClO_3$ is liquid, easily decomposed, and readily soluble in water. All the salts deflagrate when heated on charcoal, and are decomposed on ignition into chloride and O_2.

Acetates.—The normal salts are all soluble in water, although many are decomposed by boiling their solutions into insoluble basic salts. The salts are all decomposed by ignition; aceton, C_3H_6O, is almost always one of the products of decomposition, and generally $HC_2H_3O_2$. Salts of Grs. I. and II. give a residue of carbonate, the rest either metal or oxide, generally mixed with C. $Fe_2(C_2H_3O_2)_6$ gives a deep red solution, which on boiling deposits all the Fe_2 as a brown basic salt insoluble in water.

COURSE OF ANALYSIS.

PRELIMINARY EXAMINATION.

The physical properties of the substance under examination must first be carefully noted. A solid must, if possible, be reduced to fine powder; a portion of a liquid should be evaporated to dryness, and the residue, if any is left, powdered. A small quantity only is needed for each test.

Heat in a Bulb Tube.

Water is given off.—Crystal water usually given off with fusion, water of constitution without; water mechanically enclosed often with decrepitation. If the

water has an alkaline reaction, H_4N is present; if an acid reaction, some volatile acid as H_2SO_4, HCl, HNO_3, etc.

Gas escapes.—O_2 shows presence of nitrates, chlorates, or dioxides; a glowing match kindles.

CO_2 shows presence of carbonates, or certain oxalates; a drop of CaO_2H_2 + Aq rendered turbid.

CO shows presence of $H_2C_2O_4$ or some of its salts; burns with a blue flame.

H_2S shows presence of hydrous sulphide; recognized by its odor.

CN formed from cyanides decomposed by heat; recognized by odor, or burning with crimson flame.

NO_2 shows presence of nitrates; recognized by orange red color, and odor.

Cl_2, Br_2 or I_2 liberated from chlorides, bromides or iodides which are decomposed by heat.

H_3N usually shows the decomposition of an H_4N salt; recognized by test paper, and odor.

SO_2 often formed by decomposition of sulphates.

Sublimate formed.

S sublimes from many sulphides in red brown drops; solidifies yellow on cooling.

I_2 from many iodine compounds; vapor violet, the sublimate black.

H_4N. Most salts give white crystalline sublimates.

Hg and some of its compounds. Hg white metallic globules; HgS black, turns red when rubbed; $HgCl_2$ melts and sublimes white, Hg_2Cl_2 sublimes without melting. HgI_2, red, sublimes yellow, turns red when rubbed.

As and some of its compounds. As gives a metallic

mirror, As_2O_3 a crystalline sublimate; As_2S_3 sublimes reddish yellow when hot, yellow when cold.

Sb_2O_3 melts and sublimes in needles.

$H_2C_2O_4$ sublimes in part, white and crystalline.

Residue left with change of color.—A black residue may be due to the formation of a black oxide, or to carbonization showing the presence of an organic acid or other organic matter. In the latter case a characteristic odor is usually evolved. If the residue effervesces with acids, while the original substance did not, it shows the presence of acetates, tartrates, or oxalates of Grs. I. and II. The following changes of color are common. The residue

Yellow	while hot	White	when cold	ZnO
Red brown	" "	Yellow	" "	PbO
Red brown	" "	Pale yellow	" "	Bi_2O_3
Black	" "	Red	" "	Fe_2O_3

Heat on charcoal in inner blowpipe flame.—Many of the reactions of the closed tube are repeated. If the odor of SO_2 is perceived sulphides are probably present. A garlic odor shows presence of As.

Deflagration.—Shows presence of nitrates or chlorates.

Substance melts and runs into the charcoal. Salts of Gr. I.

Residue white; infusible, but luminous when heated, Gr. II., Zn, Al_2 or SiO_2. The residue must then be moistened with $Co(NO_3)_2$ + Aq and again heated in the outer flame. If the residue becomes colored, blue shows Al_2; green Zn; flesh colored, Mg; blue green, Sn. Phosphates and silicates also give a blue color.

Residue colored or metallic, with or without a coating upon the charcoal. In this case some of the substance must be mixed with Na_2CO_3 and heated in the inner blowpipe flame on charcoal. The color of the coating around the assay, and the nature of the metallic globule must be noted. If no one large globule can be obtained, the charcoal under the assay must be cut out and ground up with water in a mortar. The charcoal can readily be washed away and the metal left, in spangles, if malleable. The presence of As shown by garlic odor. The character of the metallic globules of the reducible metals and the colors of the coating on the charcoal are as follows:

ON CHARCOAL WITH Na_2CO_3.

	GLOBULE.	COATING. Hot.	Cold.
Bi	Brittle	Dark orange	Lemon yellow
Sb	"	White	White
Ag	Malleable	(Dark red)	
Sn	"	Pale yellow	White
Pb	"	Orange yellow	Yellow
Cu	"		
Zn		Yellow	White
Co		Red brown	Red brown
As			White
Co, Ni, Fe	Reduced but not fused.		

Examination with Borax.

A small quantity of the substance is melted into a

borax bead upon platinum wire. It should first be heated in the outer blowpipe flame, afterwards in the inner flame, the colors of the bead, both hot and cold, being carefully noted. An excess of substance must be avoided. The colors of the various beads, both hot and cold, in the inner and outer flames, are as follows:

BORAX BEADS.

	OUTER FLAME.		INNER FLAME.	
	Hot.	Cold.	Hot.	Cold.
Cu	Green	Blue	Colorless	Red opaque
Co	Blue	Blue	Blue	Blue
Ni	Violet	Red brown	Gray	Gray
Fe	Red	Yellow	Bottle green	Bottle green
Mn	Violet	Amethyst	Colorless	Colorless
Cr	Green	Green	Green	Green

Flame Colorations.

The coloration given by the substance to the flame of the lamp often gives more or less positive indications. The substance is introduced into the edge of the flame on platinum wire.

Red flames. K, violet; Li, carmine; Sr, crimson; Ca, orange red.

Yellow flames. Na.

Green flames. Cu (most salts) bright green; Ba, yellow green; H_3BO_3 pale green.

Blue flames. $CuCl_2$, bright blue; Pb, As pale blue.

Examination with H_2SO_4.

On heating the substance with strong H_2SO_4 the

presence or absence of certain acids may be established. If, on adding H_2SO_4, $HClO_3$ is found present, heat must not be applied.

HNO_3, HCl, HF, H_2S, CO_2 are liberated from their compounds. SO_2 shows presence of sulphites or hyposulphites; CO of oxalates or cyanides. $HC_2H_3O_2$ set free and recognized by odor. Br_2 and I_2 liberated from bromides and iodides, Cl_2O_4 from chlorates. Tartrates blacken.

SOLUTION.

Treatment with Water.

The substance in fine powder must be treated with water, first cold then hot. Most salts are more readily soluble in hot water than in cold; in a few cases the reverse is true, and some salts, though soluble in cold water, are decomposed by boiling water into insoluble basic salts. Salts of Bi, and some salts of Sb, Hg and Hg_2 are thus decomposed even by cold water.

After boiling for some time, if a portion remains undissolved, it must be collected upon a filter, washed and treated with acids. If there be any doubt whether even a part of the substance is soluble, a few drops of the filtrate must be evaporated on platinum foil.

The reaction of the aqueous solution should be tested, or, if the substance under examination is liquid, the reaction of the original solution.

An alkaline reaction shows the presence of Gr. I. or II. An acid reaction may be due to the presence of a free acid or acid salt, or due to the presence of a neutral

salt with acid reaction. In the first case a drop of Na_2CO_3 + Aq gives no precipitate, or the precipitate which is formed redissolves; in the second the turbidity is usually permanent.

Treatment with Acids.

For the solution of a substance insoluble in water HCl + Aq, HNO_3 or a mixture of the two (aqua regia) is used. A solution in HCl + Aq is much the best for subsequent work.

Many substances are soluble in dilute acids, though insoluble in strong, many soluble only in strong, and again many, that are not attacked by dilute acids, are decomposed, though not dissolved, by stronger acids, so that solution can only be effected by treatment with strong acids and subsequent dilution. The substance should therefore be boiled successively with HCl + Aq, HNO_3 and HCl + Aq with HNO_3, using first dilute, then strong, and finally adding water to that which has been boiled with strong acid.

Effervescence may show CO_2 present, or if HCl + Aq is used H_2S or SO_2. With HCl + Aq HCN is often set free from insoluble cyanides, or Cl_2 is evolved if dioxides or chromates are present. S or gelatinous H_4SiO_4 are also often separated. Unless As or Sb may be present, the solution should be freed from any great excess of acid by evaporation. It is much better, in any case, to avoid an excess from the first, taking care also that the solution be properly diluted before beginning the analysis. HCl + Aq and HNO_3 together dissolve by converting into chlorides.

If the substance is a metal or alloy, as will appear in the preliminary examination, it should be treated at once with hot HNO_3—, 1 part strong acid to 3 of water. Sb and Sn are oxidized to SnO_2 and Sb_2O_3 (Sb_2O_4) insoluble in water, or dilute HNO_3, the other metals are found in solution. As many nitrates are insoluble in strong HNO_3, though readily soluble in water, care must be taken not to mistake the crystalline nitrates for oxides of Sn or Sb. The insoluble residue may contain a part of any As present.

Treatment of Substances Insoluble in Water or Acids.

The most common substances insoluble in water or acids are : $BaSO_4$, $SrSo_4$, ($CaSO_4$), $PbSO_4$; the [illegible]s of acids of Gr. II., except Ag_2S ; ignited Al_2O_3, Cr_2O_3 or SnO_2 ; SiO_2 and many silicates ; CaF_2, S and C.

S is recognized in the preliminary examination. C is present if the substance is black, and part of it burns before the blowpipe. If Pb and Ag have not been found in the preliminary examination, special tests must be made for their presence. Ag may be found, if present, by warming the substance with KCN + Aq, which dissolves all the Ag salts insoluble in acids, and testing the filtrate with $(H_4N)_2S$ + Aq. To test for Pb, warm the substance with $H_4NC_2H_3O_2$ + Aq, which dissolves $PbSO_4$, and add to the filtered solution $(H_2N)_2S$ + Aq. If Ag or Pb are present they must be removed by successive treatment with $H_4NC_2H_3O_2$ + Aq, and KCN + Aq. If S is also present, it must be volatilized in a porcelain crucible after the removal of Pb and Ag. If

S is present, cold $KCN + Aq$ must be used for the removal of Ag.

The substance free from Ag, Pb and S, may then be mixed with 2 parts Na_2CO_3, 2 parts K_2CO_3, and 1 part KNO_3, and heated to quiet fusion in a platinum crucible. From the cooled mass water then dissolves alkaline salts of the acids present, and the bases are left as carbonates, soluble in $HCl + Aq$, after thorough washing. Al_2 is found in solution, and Cr_2 as chromate. To find the acids of the insoluble Ag salts, $NaOH + Aq$, dilute, will decompose the ferro- and ferricyanide, sodic salts of those acids going into solution by boiling; AgCl, AgBr, AgI and AgCN are reduced by Zn and dilute H_2SO_4; in the solution HCl, HBr, HI and HCN may be found. If the members of Gr. I. must be looked for in silicates, fuse with 4 parts of BaO_2H_2.

Some substances insoluble, or slowly soluble, in acids, may be decomposed with advantage by $NaOH + Aq$. The insoluble ferrocyanides and ferricyanides are decomposed by hot $NaOH + Aq$, into sodic salts of the acids and insoluble or soluble hydrates. The solution may therefore be examined for Pb, Zn and Al_2, and, after their removal, for the acids, although it must be remembered that $H_6Fe_2(CN)_{12}$ in the alkaline solution is readily converted into $H_4Fe(CN)_6$ by H_2S. The portion insoluble in $NaOH + Aq$ may be dissolved in acids and tested as usual.

The three portions of any substance, that soluble in water, that soluble only in acids, and that insoluble in water and acids, must be separately examined. The larger portion should first be analyzed, inasmuch as a

knowledge of its constitution may greatly facilitate the analysis of the smaller portions.

DETECTION OF BASES.

The bases may be divided according to their behavior with reagents into six groups, and, for convenience in analysis, these groups are separated from each other by general reagents before proceeding to test for the individual members of each group.[1] In an acid solution H_2S precipitates only members of Grs. V. and VI. The precipitation is complete, unless the solution is very strongly acid, in which case more or less Pb and Cd remain in solution. The sulphides of the two groups are separated by an alkaline solution, the sulphides of Gr. V. being insoluble, those of Gr. VI. soluble, but precipitated by the addition of acid. As the $HCl + Aq$, best used to acidify the solution, precipitates $AgCl$, Hg_2Cl_2 and $PbCl_2$ (partially), it is more convenient to separate these by filtration, and test for them apart. The members of Grs. III. and IV. are not precipitated by H_2S in a solution acidified with $HCl + Aq$, but are precipitated by $(H_4N)_2S + Aq$ in an alkaline solution—Gr. III. as hydrates, Gr. IV. as sulphides. Grs. V. and VI. are also precipitated by $(H_4N)_2S + Aq$, though the precipitate of Gr. VI. redissolves in an excess. Grs. V. and VI. must therefore be removed before precipitating Grs. III. and IV. It is more convenient not to separate Gr. III. as a whole from Gr. IV., but to test the general precipitate for members of both groups. The members of Gr. II. are not precipitated by H_2S or $(H_4N)_2S + Aq$, and are distinguished from Gr.

[1] Compare table of bases on page 1.

I. by the insolubility of their carbonates. $(H_4N)_2CO_3 + Aq$ precipitates Ba, Sr and Ca as carbonates, but as Mg is not precipitated as carbonate in presence of H_4N salts, it is more convenient to make a special test for its presence, and remove it after the H_4N salts have been expelled by ignition. $(H_4N)_2CO_3 + Aq$ precipitates most of the members of Grs. VI.–III., and these groups must therefore be removed before the precipitation of Gr. II. Members of Gr. I. are precipitated by no general reagent, but are left in solution after the removal of the higher groups. Since H_4N salts are used as reagents, tests for H_4N must be made in the original solution.

GROUPS V. and VI. Ag, Hg_2, Pb, Hg, Cu, Bi, Cu; As, Sb, Sn, Sn^{IV}.

To the solution add $HCl + Aq$. If a white precipitate[1] falls, it may contain AgCl, Hg_2Cl_2 and $PbCl_2$. Filter, wash the precipitate with a little cold water, and set aside the filtrate. The precipitate must then be washed with hot water; AgCl and Hg_2Cl_2 are insoluble, $PbCl_2$ is dissolved, if present, and by adding dilute H_2SO_4 to the solution $PbSO_4$ is precipitated. The residue, which may consist of AgCl and Hg_2Cl_2, is next treated on the filter with $H_4NOH + Aq$. Hg_2Cl_2, if present, is converted into black insoluble $[Hg_2]_2H_4N_2Cl_2$, and AgCl is dissolved. To the

[1] If the solution is alkaline, on the addition of $HCl + Aq$ As_2S_3, Sb_2S_3 or SnS_2 may be precipitated; cyanides dissolved in $KCN + Aq$ may be thrown down; gelatinous H_4SiO_4 separated, or S from alkaline sulphides. CO_2, H_2S, SO_2 and HCN may be set free. AgCl is soluble in $Hg(NO_3)_2 + Aq$, but is precipitated by the addition of $H_4NC_2H_3O_2 + Aq$.

H_4NOH [1] + Aq which has run through the filter is then added HNO_3 in excess; if Ag is present, AgCl is precipitated, white and curdy, or, if in small quantity, opalescent.

To the filtrate from the precipitate caused by HCl + Aq, add H_2S + Aq, or better, pass into it H_2S; warm for some time, adding H_2S + Aq until the solution smells strongly of it after shaking, and filter. The filtrate, which may contain Grs. I.–IV. is set aside; the precipitate may contain PbS, HgS, CuS, Bi_2S_3, CdS, As_2S_3, Sb_2S_3, SnS and SnS_2. It must be washed with hot water until $AgNO_3$ gives no precipitate of AgCl in the wash water, and then gently warmed with very little yellow $(H_4N)_2S$ + Aq. The sulphides of Gr. VI. are thus dissolved. Filter and set the filtrate aside to be examined for members of Group VI. The precipitate, which may contain PbS, HgS, CuS, Bi_2S_3 and CdS, after being well washed, is boiled with dilute HNO_3. HgS alone is insoluble, although the S which separates is often colored with a little of one of the other sulphides, and a black residue must therefore be tested for Hg. The residue is filtered off, dissolved in HCl + Aq with the addition of a very little $KClO_3$, and bright bits of Cu wire put into the solution. Hg, if present, is deposited on the Cu, and when dried may be sublimed in a bulb tube. The HNO_3 solution filtered from HgS or separated S may contain the nitrates of Pb, Cu, Bi and Cd. If Pb has already been found, it must be removed, and if not found, it may yet be present in quantity too small to be precipitated by HCl + Aq. The solution must be

[1] If $PbCl_2$ is not completely washed out, the H_4NOH + Aq is often turbid from the presence of a basic Pb salt. This does not interfere with the detection of Ag, as it dissolves readily in HNO_3.

concentrated by evaporation until the greater part of the HNO_3 has been driven off, dilute H_2SO_4 added, the solution gently warmed and allowed to stand for some time. A white precipitate is $PbSO_4$ and shows Pb present. If Pb is present, the solution must be evaporated with dilute H_2SO_4 until the HNO_3 is all expelled, water slightly acid with H_2SO_4 added, and the insoluble $PbSO_4$ filtered off. The solution now may contain Cu, Bi and Cd. Add $H_4NOH + Aq$ in excess, which precipitates BiO_3H_3 white and flocculent, if Bi is present; if the solution is blue, Cu is present. Filter from the precipitated BiO_3H_3. If the filtrate is not blue, a very small quantity of Cu may be detected by acidifying a portion with $HC_2H_3O_2$ and adding $K_4Fe(CN)_6 + Aq$ which precipitates red brown $Cu_2Fe(CN)_6$. If Cu is absent, $(H_4N)_2S + Aq$ added will precipitate yellow CdS. If Cu is present, precipitate CuS and CdS with $H_2S + Aq$, and boil the mixed sulphides with dilute H_2SO_4, avoiding exposure to the air. CdS, if present, is alone dissolved, and, after filtering off the undissolved CuS, may be precipitated by H_2S, or $H_4NOH + Aq$ and $(H_4N)_2S + Aq$, as yellow CdS.

The $(H_4N)_2S + Aq$ solution which may contain Gr. VI. is acidified with dilute $HCl + Aq$. The sulphides are thus precipitated mixed with S. If too much $(H_4N)_2S + Aq$ was not used for solution, the presence of the sulphides is readily recognized. The precipitate, which may contain As_2S_3, Sb_2S_3 and SnS_2,[1] is collected on a filter and washed, then treated in the cold with $(H_4N)_2CO_3 + Aq$. As_2S_3 dissolves and may be precipi-

[1] Brown SnS dissolved in yellow $(H_4N)_2S + Aq$ is precipitated by $HCl + Aq$ as yellow SnS_2.

tated from the filtered solution by acidifying with $HCl + Aq$ as yellow As_2S_3, if As is present. In order to confirm the presence of As, the precipitate must be thoroughly dried, mixed with dry KCN and Na_2CO_3, and the mixture heated in a bulb tube; As, if present, is sublimed as a metallic mirror.

The residue insoluble in $(H_4N)_2CO_3 + Aq$ may contain Sb_2S_3 and SnS_2. It is dissolved in strong $HCl + Aq$, with the addition of a little $KClO_3$, if necessary; any large excess of $HCl + Aq$ must be avoided. The solution is diluted and into it are put bits of platinum foil and Zn in contact. When the evolution of H_2 has ceased, Sb and Sn, if present, are found deposited upon the foil, Sb black, and Sn silver white. The foil must be carefully washed and warmed with $HCl + Aq$. Sn, if present, is dissolved as $SnCl_2$, which may be recognized in solution by adding $HgCl_2 + Aq$; Hg_2Cl_2 being precipitated, often gray from Hg.[1] Sb may be recognized by the black color of the foil. If confirmation is needed, it may be dissolved in $H_2C_4H_4O_6 + Aq$ with the addition of a few drops of HNO_3; from this solution H_2S precipitates, after addition of $HCl + Aq$, orange, Sb_2S_3 if Sb is present.

Groups III. and IV.—Al_2, Cr_2, Fe_2, Fe, Ni, Co, Mn, Zn, and phosphates and oxalates soluble in acids only.

To the filtrate from the general precipitate of Grs. V. and VI., or to the solution found not to contain Grs. V. and VI., add $H_4NCl + Aq$ and $H_4NOH + Aq$ in slight excess; heat almost to boiling, add $(H_4N)_2S$ and keep

[1] $(SnCl_2 + 2HgCl_2 + Aq) = Hg_2Cl_2 + (SnCl_4 + Aq)$.
$(SnCl_2 + HgCl_2 + Aq) = Hg + (SnCl_4 + Aq)$.

warm for some time. The precipitate is more granular if the solution is shaken well in a corked flask. Filter as rapidly as possible and wash with hot water, best with addition of a little $(H_4N)_2S$ + Aq. The filtrate, which may contain Grs. I. and II.,[1] must be concentrated by evaporation, filtered if necessary, and set aside. The color of the precipitate gives some indication of what is present. It may contain $Al_2O_6H_6$, $Cr_2O_6H_6$, FeS, MnS, ZnS, NiS, or CoS, together with phosphates or oxalates of Al_2, Cr_2 and Gr. II., and must be tested for all, if it is black. First treat with cold dilute HCl + Aq; NiS and CoS alone are insoluble, the rest go into solution. If a black residue remains Ni or Co, or both, are present. The residue must be collected on a filter and tested for Co with borax. A blue bead in the inner and outer flames shows Co is present, and Ni may be. If Co is absent and the bead gives the Ni reactions, the black residue was NiS. If Co is present, dissolve in HCl + Aq and HNO_3, add NaOH + Aq in excess and filter. Dissolve the hydrates thus obtained in as little as possible concentrated KCN + Aq, add NaOH + Aq and Br_2 + Aq. On boiling Ni, if present, is precipitated as $Ni_2O_6H_6$, Co remains in solution as $Na_6Co_2(CN)_{12}$.

The solution in HCl + Aq, filtered from NiS or CoS, if a residue was left, is boiled until H_2S is all expelled, a little HNO_3 is added, the solution again boiled till the greater part of the acid is driven off and then diluted with

[1] If Ni is present more or less NiS is dissolved in the excess of $(H_4N)_2S$ + Aq, especially if much H_4NOH + Aq is added; the filtrate is then brown or black. By evaporating and acidifying with $HC_2H_3O_2$ or HCl + Aq, NiS is precipitated.

water. If it is not already known whether H_3PO_4 and $H_2C_2O_4$ are present or not, this must now be determined.

If H_3PO_4 and $H_2C_2O_4$ are absent, neutralize the little free acid in the solution with Na_2CO_3, care being taken that no permanent precipitate is formed, then add $BaCO_3$ in the cold and allow the whole to stand for some time, stirring occasionally. The precipitate may contain $Al_2O_6H_6$, $Cr_2O_6H_6$ or $Fe_2O_6H_6$ together with the excess of $BaCO_3$, the filtrate may contain Mn or Zn with $BaCl_2$. Dissolve the precipitate collected on a filter in dilute HCl + Aq, warm gently and add H_4NOH + Aq which will precipitate as hydrates Fe_2, Al_2 and Cr_2, if present. This precipitate must be collected on a filter, washed, dried and dissolved in a little strong HNO_3. The solution is then boiled with a few crystals of $KClO_3$ for several minutes, and NaOH + Aq added in excess. $Fe_2O_6H_6$ is precipitated, if Fe is present, and the solution may contain $Al_2O_6Na_6$ and Na_2CrO_4. In a part of the solution Al_2 may be precipitated by adding H_4NCl + Aq as $Al_2O_6H_6$,[1] or, after acidifying with HNO_3, H_4NOH + Aq causes the same precipitate; another portion of the solution is acidified with $HC_2H_3O_2$ and $BaCl_2$ + Aq added, which precipitates $BaCrO_4$, if Cr_2 is present. If NaOH + Aq precipitates $Fe_2O_6H_6$, the original solution must be tested by adding to a small portion $K_6Fe_2(CN)_{12}$ + Aq, which gives blue $Fe_3Fe_2(CN)_{12}$, if Fe is present;

[1] NaOH often contains silicate, and gelatinous H_4SiO_4 is then precipitated here. It may be distinguished from $Al_2O_6H_6$ by its insolubility in $H_4NNaHPO_4$ bead, and readily separated from it by fusion with $KHSO_4$, treatment with HCl + Aq and precipitation of $Al_2O_6H_6$ from the solution, if present, by H_4NOH + Aq.

to another portion add $K_4Fe(CN)_6$ + Aq, which gives blue $[Fe_2]_2[Fe(CN)_6]_3$, or KCNS giving blood red solution of $Fe_2(CNS)_6$, if Fe_2 is present.

Small quantities of Cr_2 may also be detected by fusing the dried precipitate with a mixture of equal parts of Na_2CO_3 and KNO_3. If the cooled mass is boiled with water, the solution filtered and acidified with $HC_2H_3O_2$, on the addition of $Pb(C_2H_3O_2)_2$ + Aq, $PbCrO_4$ is precipitated.

The filtrate from the $BaCO_3$ precipitate, which may contain Zn and Mn, is heated to boiling and the Ba it contains completely precipitated with dilute H_2SO_4; filter from the $BaSO_4$, to the filtrate add NaOH + Aq in excess and boil. MnO_2H_2 is precipitated, if present, and the solution may contain Zn. The precipitate is collected on a filter, and a portion of it fused on platinum wire with Na_2CO_3 and KNO_3. Blue green K_2MnO_4 is formed, if the precipitate was MnO_2H_2. The NaOH + Aq solution, which may contain Zn, is acidified with $HC_2H_3O_2$ and ZnS, white, precipitated by H_2S, if Zn is present.

If H_3PO_4 and $H_2C_2O_4$ are present, the HCl + Aq solution boiled with HNO_3 and treated as before must first be tested for Ba, Sr and Ca. To a small portion add dilute H_2SO_4. If a precipitate is formed filter, and examine in the spectroscope. To the filtrate add 3 times its volume of alcohol; $CaSO_4$ is precipitated, if Ca is present, and its presence may be confirmed by dissolving the precipitate in water and throwing down CaC_2O_4 with $(H_4N)_2C_2O_4$ + Aq. To the rest of the solution add Fe_2Cl_6 + Aq cautiously till a drop of the solution gives with H_4NOH + Aq a yellowish precipitate. The solution must

then be neutralized with Na_2CO_3 + Aq, as before, and $BaCO_3$ added. The precipitate with $BaCO_3$ is examined as above, except, of course, that Fe and Fe_2 must be proved present or absent by $H_4Fe(CN)_6$ + Aq and $K_6Fe_2(CN)_{12}$ + Aq, in the original solution. The filtrate from the $BaCO_3$ precipitate may contain Ca and Mg as well as Mn and Zn. After removing Ba with dilute H_2SO_4, H_4NOH + Aq must be added, ZnS and MnS precipitated, if present, by $(H_4N)_2S$ + Aq, collected on a filter, and dissolved in HCl + Aq. They may then be separated and detected as before. The filtrate from the precipitate of ZnS and MnS may contain Ca and Mg. The Ca is precipitated as CaC_2O_4 filtered off, and the filtrate tested for Mg by adding Na_2HPO_4 + Aq.

GROUP II. Ba, Sr, Ca, Mg.

To the filtrate from the general precipitate of Grs. III. and IV., or to the solution found not to contain Grs. III.–VI., add H_4NCl+Aq,[1] if it be not already in solution, then H_4NOH + Aq in slight excess, unless the solution is already alkaline; heat almost to boiling, add $(H_4N)_2CO_3$ + Aq to complete precipitation, and filter after allowing it to stand for a few minutes.

The filtrate may contain Mg or members of Gr. I. To a small part of it add Na_2HPO_4+Aq. A white crystalline precipitate, forming only after the lapse of some time, if the solution be dilute, is $Mg_2(H_4N)_2(PO_4)_2$.[2] The rest of the filtrate is then evaporated for Gr. I.

[1] H_4NCl + Aq prevents possible precipitation of Mg.

[2] The filtrate may contain small quantities of Ba, Sr or Ca. A slight precipitate with Na_2HPO_4 may therefore not be due to presence of Mg. In a fresh portion Ba should be tested for and removed

The precipitate thrown down by $(H_4N)_2CO_3$ + Aq may contain $BaCO_3$, $SrCO_3$ or $CaCO_3$, and must be tested for all three. The carbonates are dissolved in $HC_2H_3O_2$, and to a small part of the solution $CaSO_4$ + Aq is added. An immediate white precipitate is $BaSO_4$, and shows that Ba is present,—Ca and Sr may be; a tardy precipitate is $SrSO_4$, and shows that Ba is absent and Sr present,—Ca may be ; no precipitate even on long standing shows that Ba and Sr are absent, and the original precipitate was $CaCO_3$ alone.

If Ba is present, it must be removed before testing for Sr or Ca. To the rest of the $HC_2H_3O_2$ solution is then added K_2CrO_4 + Aq in slight excess, and the precipitated $BaCrO_4$ filtered off. To the filtrate add H_4NOH + Aq in excess, warm and add $(H_4N)_2CO_3$ + Aq. The precipitate may contain $SrCO_3$ or $CaCO_3$ or both. It must be washed till all K_2CrO_4 is removed and dissolved in $HC_2H_3O_2$. To a small portion of the solution add $CaSO_4$ + Aq. A white precipitate on standing is $SrSO_4$ and shows Sr present,—Ca may be.

If Sr is present, to the rest of the $HC_2H_3O_2$ solution, from which the Ba has been removed, or in which it was originally found absent, is added, dilute H_2SO_4 in slight excess. After standing for some time $SrSO_4$ separates, mixed with $CaSO_4$, if the solution is concentrated ; on filtering $CaSO_4$ will be found in solution, if present, by adding H_4NOH + Aq in excess and $(H_4N)_2C_2O_4$ + Aq ; Ca then falls as white CaC_2O_4.

If Sr is absent, whether Ba was originally absent or was

with dilute H_2SO_4, Ca with $(H_4N)_2C_2O_4$ + Aq before accepting the precipitate with Na_2HPO_4 + Aq as a proof of the presence of Mg

removed, H_4NOH + Aq and $(H_4N)_2C_2O_4$ added to the rest of the $HC_2H_3O_2$ solution precipitates CaC_2O_4 if Ca is present.

Ba, Sr and Ca may also be distinguished by the spectroscope. Ba recognized by four green bands; Sr by one orange, two red, and one blue band; Ca best by a green and orange band.

GROUP I. Na, K, Li, HN.

The filtrate from the general precipitate of Gr. II. or the solution in which Grs. II.–VI. have been found absent, must be evaporated to dryness and ignited until H_4N salts are expelled.

If Mg was found to be absent, the residue contains only Na, K or Li, and should be tested with the spectroscope. K gives a band in the extreme red, Na a yellow band, and Li a red band between the two. The presence of Na in notable quantity is shown by the intensity and duration of the yellow flame. $NaHC_4H_4O_6$ + Aq may also be used in a cold concentrated aqueous solution of the residue as a test for K, precipitating $KHC_4H_4O_6$. NaC_2O_3 + Aq precipitates from concentrated solutions $LiCO_3$, or Na_2HPO_4 + Aq, with the addition of a little NaOH + Aq, precipitates Li_3PO_4 in a solution not too dilute.

If Mg was found present, the residue from ignition[1] must be dissolved in a little water, and BaO_2H_2 + Aq added in slight excess. The MgO_2H_2 thus precipitated is filtered out, the Ba completely precipitated from the boiling hot filtrate by dilute H_2SO_4, and the liquid freed

[1] **MgO_2H_2 not precipitated from solutions containing H_4N salts.**

from $BaSO_4$ by filtration evaporated to dryness. The residue, after the excess of H_2SO_4 has been driven off, is tested as before in the spectroscope.

To test for H_4N some of the original solution or substance must be mixed with CaO_2H_2 to a stiff paste, and gently warmed. H_3N [1] is then set free, which may be recognized by its action on moist test-paper, or by its forming white fumes of H_4NCl with HCl.[2]

DETECTION OF ACIDS.

The acids are divided into three groups, according to the solubility of the Ba and Ag salts.[3] $BaCl_2$ + Aq precipitates all the members of Gr. I. in neutral or alkaline solutions, but does not precipitate Grs. II. and III. $AgNO_3$ + Aq precipitates in HNO_3 solution only members of Gr. II., but in neutral solution almost all of Gr. I. Members of Gr. III. are precipitated by neither reagent. The acids are not separated after precipitation by the general reagents, as was the case with bases, the presence or absence of members of the groups alone being shown.

In beginning the analysis for acids, those acids, which from the nature of the bases present and the solvent used are necessarily absent, must first be considered. In a substance soluble in water no acids can be present which form insoluble salts with any of the bases found in the solution. In a substance insoluble in water and

[1] $2H_4NCl + CaO_2H_2 = CaCl + 2H_2O \div 2H_3N$.

[2] The HCl + Aq used must not fume in the air.

[3] See table of acids on page 19.

soluble in acids, the number of acids which may thus be safely excluded, as forming soluble salts with the bases is small, and it is better to look for all. In substances insoluble in water or acids, a knowledge of the bases will usually render the number of acids that must be tested for very small.

If the substance is soluble in water, the bases will generally not interfere with the detection of those acids which can be present, although in testing for $HC_2H_3O_2$ and $H_2C_4H_4O_6$ the solution cannot contain bases of Grs. III.–VI. If the substance is soluble in acids alone, the removal of the bases of Grs. III.–VI. always facilitates the detection of the acids, and is often essential. They should be removed with H_2S, $(H_4N)_2S + Aq$, $Na_2CO_3 + Aq$, $NaOH + Aq$, as the case may be, any excess of H_2S removed, and the solution made neutral, carefully boiling out CO_2, if Na_2CO_3 was used.

GROUP I. 1. M_2CrO_4, M_3AsO_3, H_3AsO_4, M_2SO_3, $M_2S_2O_3$.

These acids will have been discovered, if present, by the preliminary examination, or in the course of the analysis for bases; their presence must be confirmed by special tests. They are all decomposed by H_2S in acid solution.

Chromates.—$Pb(C_2H_3O_2)_2 + Aq$ gives yellow $PbCrO_4$, insoluble in $HC_2H_3O_2$. $AgNO_3 + Aq$ in neutral solution precipitates brick red $AgCrO_4$.

Arsenites.—H_2S precipitates As_2S_3 yellow immediately from acid solutions; $AgNO_3 + Aq$ gives in neutral solutions pale yellow Ag_3AsO_3. Further recognized in presence of H_3AsO_4 by adding a few drops of $CuSO_4$

+ Aq, then NaOH + Aq in excess; on boiling $Cu_2O_2H_2$ precipitated, orange yellow.

Arseniates.—H_2S precipitates As_2S_3 very slowly from acid solutions; $AgNO_3$ + Aq gives in neutral solutions red brown precipitate of Ag_3AsO_4. Further distinguished from arsenites by H_4NOH + Aq, H_4NCl + Ag, and $MgSO_4$ + Aq; $Mg_2(H_4N)_2(AsO_4)_2$ precipitated, easily mistaken for phosphate.

Sulphites.—Salts give off SO_2 when treated with H_2SO_4 or HCl + Aq. SO_2 recognized by smell and blackening of paper moistened with $Hg_2(NO_3)_2$ + Aq by separation of Hg. Zn and HCl + Aq liberate from solutions of sulphides H_2 mixed with H_2S. If sulphides also present, must they be removed by $ZnSO_4$ + Aq and the filtrate tested.

Hyposulphites.—From solutions H_2SO_4 orHCl + Aq evolve SO_2 with separation of S. The reaction is delayed by dilution. $Pb(C_2H_3O_2)_2$ + Aq or $AgNO_3$ + Aq give white precipitates which blacken on boiling.[1] Sulphides, if present, must first be removed with $ZnSO_4$ + Aq.

GROUP I. 2. (a) H_3PO_4, H_3BO_3, HC_2O_4, HF, M_2CO_3. H_4SiO_4, $H_2C_4H_4O_6$; (b) H_2SO_4.

By the preliminary examination H_2CO_3, $H_2C_4H_4O_6$, and H_4SiO_4 will have been found, if present. H_2CO_3 and H_4SiO_4 must be removed by HCl + Ag or HNO_3 and evaporation, if present; their presence is confirmed by special tests.

To a solution free from acids of Gr. I. 1, H_2CO_3 and H_4SiO_4 add H_4NOH + Aq to neutral or slightly alkaline reaction, then $BaCl_2$ + Aq. The precipitate may contain

[1] $PbS_2O_3 + H_2O = PbS + H_2SO_4$

the Ba salts of H_3PO_4, H_3BO_3, $H_2C_2O_4$, HF, $H_2C_4H_4O_6$ and H_2SO_4. Add dilute[1] HCl+Aq in excess; $BaSO_4$ is insoluble, the other Ba salts dissolve. If H_4NOH+Aq is added in excess to the filtered solution, $Ba_3(PO_4)_2$ and BaC_2O_4 are precipitated, if present; the other Ba salts, more or less soluble in H_4NCl+Aq, will probably not be precipitated, if present. If therefore H_4NOH + Aq causes a precipitate in the HCl + Aq solution, special tests must be made for all the acids, except H_2SO_4, whose presence or absence is already established; if H_4NOH gives no precipitate, H_3PO_4 and $H_2C_2O_4$ are absent, and for the rest special tests must be applied.

It is often advisable to add $CaCl_2$ + Aq to a fresh portion of the solution made slightly alkaline with H_4NOH + Aq. The Ca salts of H_3PO_4, H_3BO_3, $H_2C_2O_4$, HF and $H_2C_4H_4O_6$ are thus precipitated; $CaSO_4$ is not thrown down, if the solution is moderately dilute. Of these Ca salts CaC_2O_4 and CaF_2 alone are insoluble in HC H_3O_2; if the precipitate is soluble in $HC_2H_3O_2$, $H_2C_2O_4$ and HF are absent, if insoluble all may be present.

Phosphates.—In aqueous solutions H_4NOH + Aq, H_4NCl + Aq and $MgSO_4$ + Aq precipitate crystalline $Mg_2(H_4N)_2(PO_4)_2$, which appears only after some time, if the solution is dilute. To detect H_3PO_4 in salts soluble in acids alone, add a little of a HNO_3 solution of the salt to $(H_4N)_2MO_4$ dissolved in HNO_3; a yellow precipitate is formed at once, or on gently warming (not above 40°), if the solution is very dilute. H_3AsO_4 gives a similar precipitate on boiling.

[1] $BaCl_2$ is insoluble in strong HCl + Aq.

Borates.—Into a solution acid with $HCl + Aq$ is dipped a strip of turmeric paper. The paper when dried at 100° is red, the red tint changing to greenish black on moistening with Na_2CO_3+Aq.

Oxalates.—Distinguished from phosphates by the insolubility of CaC_2O_4 in $HC_2H_3O_2$, and by giving no precipitate with $MgSO_4 + Aq$ in presence of $H_4NCl + Aq$. The salts heated with strong H_2SO_4 evolve CO and CO_2. The CO may be kindled, if in sufficient quantity; dilute H_2SO_4 and MnO_2 set free CO_2. The insoluble oxalates of Gr. II. give, when boiled with a concentrated solution of Na_2CO_3, an insoluble carbonate and $Na_2C_2O_4$ in solution.

Fluorides.—The salt mixed with just enough strong H_2SO_4 to form a thick paste is warmed in a platinum crucible covered with a piece of glass. HF is set free and the glass is etched. The etching is best seen, if the glass is covered with wax, and a few scratches made through it. If Si is present, SiF_4 is evolved. Compounds of F, upon which H_2SO_4 has no action, must be fused with a mixed Na_2CO_3 and K_2CO_3, CaF_2 precipitated, and tested as before.

Tartrates.—The presence of tartrates is first recognized in the preliminary examination by charring with odor of burnt sugar. $CaC_4H_4O_6$ is distinguished by its dissolving in cold $NaOH + Aq$; when the solution is boiled the salt is thrown down as a gelatinous precipitate, which redissolves as the solution cools. In a solution acid with $HC_2H_3O_2$, $KC_2H_3O_2$ precipitates $KHC_4H_4O_6$.

Carbonates.—Salts decomposed by acids with effervescence, the escaping CO_2 precipitates $CaCO_3$ from

$CaO_2H_2 + Aq$. $HCl + Aq$ is poured upon the carbonate in a test tube, the gas allowed to collect and carefully decanted into another tube half full of $Ca_2O_2H_2 + Aq$. An excess of CO_2 dissolves $CaCO_3$ forming soluble $CaH_2(CO_3)_2$.

Silicates.—Generally recognized by the separation of gelatinous H_4SiO_4 on adding $HCl + Aq$. A solution of a silicate acidified with $HCl + Aq$ and evaporated to dryness leaves all its Si as a hard gritty powder insoluble in water or $HCl + Aq$. The powder is also insoluble in a bead of NaH_4NHPO_4; Al_2O_3 dissolves readily.

Sulphates.—Sufficiently characterized by $BaSO_4$; insoluble in dilute $HCl + Aq$. Ignited on charcoal with Na_2CO_3, in the inner blowpipe flame, Na_2S is formed, which, when moistened with water, stains Ag black.

GROUP II. HCl, HBr, HI, HCN, H_2S, $H_4Fe(CN)_6$, $H_6Fe_2(CN)_{12}$.

The presence of H_2S will have been already established, and probably that of HCl, HBr, HI and HCN. H_2S, if present, must be expelled. As the Ag salts of all the acids of Gr. I. except AgF are insoluble in water and soluble in HNO_3, acidify the solution with HNO_3 and add $AgNO_3 + Aq$. The precipitate may contain Ag salts of all the members of the group. They are soluble in $H_4NOH + Aq$, except AgI and $Ag_4Fe(CN)_6$. Further than this special tests must be made.

Chlorides.—On heating with H_2SO_4 and MnO_2 Cl_2 evolved, recognized by color, odor and bleaching power. HCl in the presence of HBr and HI may be recognized by adding to the hot solution $AgNO_3+Aq$ in quantity

insufficient to cause complete precipitation. If the filtered solution no longer contains HI or HBr, and $AgNO_3$ + Aq causes a further precipitate, HCl is present, since AgCl is last thrown down.

Bromides.—On heating with H_2SO_4 and MnO_2 Br_2 is evolved. To a solution of a bromide in a test tube add a little CS_2 or chloroform, then Cl_2 + Aq drop by drop, shaking the tube; the liberated Br_2 dissolves in the CS_2 coloring it red. If HI is also present the CS_2 is violet. Add then Cl_2 + Aq, cautiously shaking the tube, and the violet I_2 color will gradually disappear, and leave the CS_2 colored red by Br_2—more Cl_2 Aq will bleach the Br_2 color also.

Iodides.—To a neutral or slightly acid solution of an iodide add a little thin boiled starch paste, and then Cl_2 + Aq cautiously. A blue compound of I with starch is formed. The color fades with heat or with an excess of Cl_2 + Aq. Instead of Cl_2 + Aq, KNO_2 + Aq, in a solution acid with H_2SO_4, may be used to advantage, as an excess does little harm.

Cyanides.—Free HCN liberated from cyanides may be recognized by its odor (vapors poisonous). If a few drops of yellow $(H_4N)_2S$ + Aq be exposed to the vapors of HCN or added to a liquid containing HCN, H_4NCNS is formed. The $(H_4N)_2S$ + Aq or the solution is evaporated until the excess of $(H_4N)_2S$ is driven off (not heated above 100°), dilute HCl + Aq added and blood red $Fe_2(CNS)_6$ formed in solution by adding Fe_2Cl_6 + Aq. To a solution of HCN, or a cyanide, add successively Fe_4SO + Aq, Fe_2Cl_6 + Aq, NaOH + Aq and HCl + Aq in excess: there is formed blue insoluble $[Fe_2]_2[Fe(CN)_6]_3$.

Sulphides.—H_2S is liberated by $HCl + Aq$ from those sulphides which are decomposed by it. Paper moistened with $Pb(C_2H_3O_2)_2 + Aq$, best slightly alkaline, is blackened by exposure to H_2S, PbS formed. From those sulphides not attacked by $HCl + Aq$, HNO_3 or $HCl + Aq$ and HNO_3 separate S, which is yellow and often spongy, and burns to SO_2. More or less H_2SO_4 also formed.

Ferrocyanides.—Soluble salts recognized by giving on addition of $Fe_2Cl_6 + Aq$, blue $[Fe_2]_2[Fe(CN)_6]_3$. Insoluble salts boiled with $NaOH + Aq$ and the acidified solution tested with $Fe_2Cl_6 + Aq$.

Ferricyanides.—Soluble salts, recognized by adding $FeSO_4 + Aq$—best made from dilute H_2SO_4 and Fe to insure absence of Fe_2 salt. Blue $Fe_3Fe_2(CN)_{12}$ formed. Insoluble salts treated like the insoluble ferrocyanides, and the solution tested with $FeSO_4 + Aq$.

GROUP III. HNO_3, $HClO_3$, $HC_2H_3O_2$.

The acids will have been recognized in the preliminary examination; to confirm their presence special tests must be made.

Nitrates.—Treated with strong H_2SO_4 and Cu turnings give off NO, which forms orange red NO_2 with air. A better test is to mix in a test tube with a concentrated solution of $FeSO_4$. Add strong H_2SO_4 in the cold, letting it run down the side of the tube and collect at the bottom; where the two layers are in contact, a brown or black ring is formed.

Chlorates.—$HCl + Aq$ or H_2SO_4 decompose all salts, giving yellow solution and yellow green gas.

Acetates.—H_2SO_4 liberates $HC_2H_3O_2$, which may be recognized by its odor. A neutral solution of an acetate, on the addition in the cold of a few drops of Fe_2Cl_6, turns red from the formation of $Fe_2(C_2H_3O_2)_6$. On boiling the red solution, a brown basic salt is thrown down and the liquid above is colorless. Before applying this test, the bases of Grs. III.–VI. must be removed and the solution made strictly neutral.

Table showing the Solubility in Water and Acids of the more Common Salts.

	O.	H_2S.	HCl.	HBr.	HI.	HCN.	H_2CrO_4.	H_3AsO_3.	H_3AsO_4.	H_2SO_4.	H_3PO_4.
K	1	1	1	1	1	1	1	1	1	1	1
Na	1	1	1	1	1	1	1	1	1	1	1
H_4N	1	1	1	1	1	1	1	1	1	1	1
Ba	1	1	1	1	1	1 2	2	2	2	3	2
Sr	1	1	1	1	1	1	1–2	2	2	3	2
Ca	1–2	1	1	1	1	1	1–2	2	2	1–3	2
Mg	2	2	2	1	1	1	1	2	2	1	2
Al_2	2 & 3	2	2	1	1	..	..	..	2	1	2
Cr_2	2 & 3	2 & 3	1 & 3	1&3	1	2	2	.	2	1 & 2	2
Fe_2	2	2	1	1	1	..	1	2	2	1	2
Fe	2	2	1	1	1	2–3	..	2	2	1	2
Zn	2	2	1	1	1	2	1	..	2	1	2
Mn	2	2	1	1	1	2	1	2	2	1	2
Ni	2	2	1	1	1	2–3	2	2	2	1	2
Co	2	2	1	1	1	2–3	2	2	2	1	2
Ag	2	2	3	3	3	3	2	2	2	1–2	2
Pb	2	2	1–3	1–3	1–2	2	2–3	2	2	2–3	2
Hg_2	2	2	2–3	2–3	2		2	2	2	1–2	2
Hg	2	2	1	1	2	1	1–2	2	2	1	2
Bi	2	2	1–2	1–2	2	..	2	..	2	1	2
Cu	2	2	1	1	1	2	1	2	2	1	2
Cd	2	2	1	1	1	2	2	..	..	1	2
Sn	2	2	1	..	1	..	2	..	..	1	2
Sn^{IV}	2 & 3	2	1	..	1	..	..	..	2	..	2
Sb	2	2	1–2	1–2	1–2	..	2	2	2	2	1–2

	H_3BO_3.	$H_2C_2O_4$.	HFl.	H_2CO_3.	H_4SiO_4.	$H_2C_4H_4O_6$.	$H_4Fe(CN)_6$.	$H_6Fe_2(CN)_{12}$.	HNO_3.	$HClO_3$.	$HC_2H_3O_2$.
K	1	1	1	1	1	1	1	1	1	1	1
Na	1	1	1	1	1	1	1	1	1	1	1
H_4N	1	1	1	1	..	1	1	1	1	1	1
Ba	2	2	2–3	2	2	2	1–2	..	1	1	1
Sr	2	2	2–3	2	2	2	1	..	1	1	1
Ca	2	2	2–3	2	2	2	1	1	1	1	1
Mg	1–2	2	2–3	2	2	1–2	1	1	1	1	1
Al_2	2	2	1	..	2–3	1	..	..	1	1	1
Cr_2	2	1–2	1	..	2	1	..	..	1	1	1
Fe_2	2	2	1	..	2	1	3	1	1	1	1
Fe	2	2	1–2	2	2	1–2	3	3	1	1	1
Zn	2	2	1–2	2	2	2	2–3	2	1	1	1
Mn	2	1–2	2	2	2	1–2	2	3	1	1	1
Ni	2	2	1–2	2	2	2	3	3	1	1	1
Co	2	2	1–2	2	2	1	3	3	1	1	1
Ag	2	2	1	2	..	2	3	3	1	1	1
Pb	2	2	2	2	2	2	2	1–2	1	1	1
Hg_2	..	2	..	2	..	1–2	..	..	1	1	1–2
Hg	..	2	1–2	2	..	2	..	..	1	1	1
Bi	2	2	1	2	..	2	..	..	1	1	1
Cu	2	2	2	2	2	1	3	..	1	1	1
Cd	1–2	2	1–2	2	2	1–2	..	..	1	1	1
Sn	2	2	1	..	..	2	3	3	..	1	1
Sn^{IV}	..	1	1	..	..	..	3	..	..	..	1
Sb	..	2	1	..	..	2	..	..	..	..	..

1 = soluble in water; 2 = soluble in acids only; 3 = insoluble in water or acids; 1–2 = sparingly soluble in water, readily in acids; 1–3 = sparingly soluble in water and acids; 2–3 = sparingly soluble in acids only.

2